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(54) Title: ISOMERIZATION OF BISPHENOLS

(57) Abstract

A catalyst useful for the condensation of an aldehyde or ketone starting material with a phenol was an insoluble mercaptosulfonic acid compound. The heterogeneous catalysts comprise catalytically-active species represented by formula (II). L was an optional linking group and - was a bond, which catalytically-active species was attached by the bond - to an insoluble organic or inorganic support; or a catalytically-active species represented by formula (III), wherein L' was an optional linking group, - was a bond and θ' and θ'' were residues of θ, and a and b were independently selected from integers equal to or greater than 1. These catalysts isomerize o,p-bisphenols to p,p-bisphenols.

$$(HS)_a - \theta' - (SO_3H)_b \qquad (II)$$
$$|$$
$$L$$
$$|$$

$$(HS)_a \quad (SO_3H)_b$$
$$\backslash \quad / \qquad (III)$$
$$-[\quad \theta'' - L'] -$$

ISOMERIZATION OF BISPHENOLS

This invention relates to preparation of polyphenols, more particularly to the preparation of polyphenols from ketones or aldehydes and phenols.

5   Acid-catalyzed condensation of phenols with aldehydes or ketones was well known. Acid catalysts include acidic ion exchange resin catalysts and soluble acid catalysts. Soluble acid catalysts can be, for example, hydrogen chloride, sulfuric acid, hydrochloric acid, phosphoric acid, hydrobromic acid, nitric acid, dimethyl sulfate, sulfur dioxide,

10   4-toluenesulfonic acid, boron trifluoride, alkanesulfonic acids, boron trifluoride complexes and other acid-acting compounds, including compounds which were hydrolyzed by water to form acids; for example, aluminum chloride, sulfonyl chloride and phosgene.

A number of compounds were known to promote such an acid-catalyzed

15   condensation. These promoters include mercaptan groups that were either free or bound to a resin. Alkyl mercaptans and bis-mercaptoethanolamine were examples of reported promoters.

It has been proposed by Scriabine et al., (U. S. Patent No. 2,923,744) to produce Bisphenol A using sulfuric acid, promoted by

20   mercaptoalkanesulfonic acids or salts or corresponding sulfonate esters at a level of 0.1 to 5 percent by weight of the base charge, to catalyze condensation of acetone and phenols, when used in amounts of 0.1 to 5 percent by weight based on total charge. Sulfuric acid was used in amounts of 2 moles per mole of acetone.

25   Riemann et al., (U.S. Patent No. 4,675,458) have proposed making 9,9-bis-(4-hydroxyphenyl)fluorene in the presence of sulfuric acid, preferably concentrated sulfuric acid, and a mercaptan, particularly 3-mercaptopropionic acid, as a promoter.

Massirio et al., (U.S. Patent No. 5,248,838) have disclosed the use

30   of a combination of methanesulfonic acid and a mercaptan/mercaptoalkanoic acid for catalyzing the condensation of phenols with fluorenone. High levels of methanesulfonic acid with respect to the feed and the mercaptan/mercaptoalkanoic acid, were used. The reactions can be run in halogenated hydrocarbon solvents.

35   Bottenbruch et al., (U. S. Patent No. 4,996,373) have proposed a process for producing dihydroxyaryl compounds from carbonyl compounds and

phenols under high pressure, in the presence of various catalysts, including sulfonic acid resins. Catalysts containing sulfhydryl functionality, for example, ion exchangers treated with mercapto compounds, have been disclosed for this use.

5   Meyer et al., (U.S. Patent No. 4,387,251) have proposed processes for making 4,4'-dihydroxydiphenyl alkanes using aromatic sulfonic acids as condensing agents. Mercapto groups were included within the definition of R₃ and were characterized as being inert. Freitag et al., (U.S. Patent No. 5,210,328) disclose using the same types of sulfonic acid catalysts for
10   making cycloalkylidene bisphenols.

        Jansen (U.S. Patent No. 2,468,982) has proposed preparation of bisphenols using anhydrous hydrogen chloride in combination with a mercaptoalkanoic acid, which may be formed in situ by reaction of a mercapton with the ketone, as condensing agent.

15   Knebel et al., (U.S. Patent No. 4,931,594) disclose the use of large amounts of sulfonic acid resin, mixed with uncombined 3-mercaptopropionic acid, to cause the condensation to occur.

        It has been proposed in British Patent No. 1,185,223 to use a mixture of insoluble resins, one as a sulfonic acid resin and the other a
20   resin containing mercapto groups, for making bisphenols.

        Randolph et al., (U.S. Patent No. 5,212,206) disclose a catalyst, made by treating a sulfonated ion-exchange resin with a dialkylaminomercaptan. Other references, representative of references on modification of sulfonic acid ion-exchange resins, include Wagner (U.S.
25   Patent No. 3,172,916). McNutt et al., (U.S. Patent No. 3,394,089), Faler et al., (U.S. Patent Nos. 4,455,409; 4,294,995 and 4,396,728); Heydenrich et al., (U.S. Patent No. 4,369,293); Berg et al., (U.S. Patent No. 5,302,774) and Maki et al., (U.S. Patent No. 4,423,252). The reactive catalysts generally include mercapto-functions attached to a sulfonic acid
30   group in the form of a sulfonamido or ammonium sulfonate salt.

        Shaw (U.S. Patent No. 4,859,803) discloses preparing bisphenols from phenol and a ketone in the presence of an acidic (sulfonic acid) ion-exchange resin and a mercaptan. The mercaptan being added at particular locations of a specified reactor configuration to prevent the formation of
35   cyclic dimers.

        Li has disclosed (U.S. Patent No. 4,825,010) isomerization of by-products of condensates of phenols and ketones, using a catalytic

amount of acidic sulfonated cationic-exchange resin having sulfonic acid
sites ionically bonded to alkylmercaptoamines. Other patents by Li (U.S.
Patent Nos. 4,822,923 and 5,001,281) further suggest the state of the art
of using ion-exchange resins to isomerize by-products of bisphenol synthe-
5   ses.

        Powell et al.,. (U.S. Patent No. 5,105,026) disclose using acidic
ion-exchange resins to isomerize undesirable products of bisphenol
synthesis to desirable products, for example, to Bisphenol A. Morgan (U.S.
Patent No. 3,546,165) has disclosed condensation of phenol with various
10   ketones, including fluorenone and indanone, using high levels of
hydrochloric acid or hydrogen chloride, in the presence of minor amounts
of 3-mercaptopropionic acid. The products were used for the preparation
of polyester resins.

        Szabolcs (U.S. Patent Nos. 4,467,122 and 4,503,266) discloses
15   washing crude product, containing BHPF, from a hydrochloric acid/zinc
chloride catalyzed process, to remove HCl, $ZnCl_2$ and excess phenol, prior
to recrystallization from dichloroethane. See also the abstract for DE
OLS 2,948,222 (July 30, 1981).

        Korshak et al., (SU 172,775) disclose washing a mixture of phenol,
20   BHPF and HCl with water, after which phenol was removed by distillation.

        The following references disclose the preparation of resins,
containing sulfonic acid functionality, introduced either by
copolymerization or by sulfonation after polymerization:

                U.S. Patent No. 3,205,285   Turbak et al.
25   U.S. Patent No. 3,366,711   Mazzolini et al.

                U.S. Patent No. 3,426,104   Masson

                U.S. Patent No. 4,587,304   Thaler et al.

                U.S. Patent No. 4,764,557   Eichenauer et al.

        Trapasso (U.S. Patent No. 3,706,707) discloses the preparation of
30   adducts from a polymerized cyclic ether and a sultone. Dean (U.S. Patent
No. 4,568,724) was of similar interest with respect to reaction products
from an EPDM rubber and a sultone.

        Welch (U.S. Patent No. 3,029,221) and Niwa et al., (U.S. Patent No.
4,912,170) disclose processes for modifying polystyrene resins.

35   It was an object of this invention to provide a process for the
condensation of aldehydes or ketones with phenols, to achieve high yields

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of preferred bis-(4-hydroxyaryl) isomers with low reaction times while avoiding use of strong inorganic acids.

Further objects of the invention include the development of processes for the synthesis of polyphenols, characterized by high yields

5   of high purity products under reaction conditions, which were not corrosive to vessels in which the processes were conducted. In addition, avoiding the use of sulfuric acid, eliminates the possibility of side reactions, including sulfonation of phenols.

In one aspect, this invention relates to a process for the

10 condensation of an aldehyde or ketone starting material with a phenol, unsubstituted in at least one position, comprising reacting the aldehyde or ketone starting material with the phenol in a reaction mixture in the presence of a soluble or insoluble mercaptosulfonic acid compound under conditions sufficient to bring about formation of a geminal bisphenolic

15 moiety at each aldehyde or ketone moiety in the starting material; provided that the soluble mercaptosulfonic acid compound was characterized by the formula
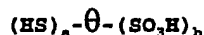
$$(HS)_a-\theta-(SO_3H)_b$$

wherein θ was an alkylene, cycloaliphatic, arylene, alkylenearylene,

20 alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue and a and b were independently selected from integers from 1 to 20; and

The insoluble mercaptosulfonic acid comprises a catalytically-active species represented by the formula

25
$$(HS)_a-\theta'-(SO_3H)_b$$
$$|$$
$$L$$
$$|$$

in which θ' was an alkylene, cycloaliphatic, arylene, alkylenearylene,

30 alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were independently selected from integers from 1 to 20; L was an optional linking group and - was a bond, which catalytically-active species was attached by the bond - to an insoluble organic or inorganic support; or a catalytically-active species represented by the unit formula

35
$$(HS)_a \quad (SO_3H)_b$$
$$\backslash \quad /$$
$$-[\quad \theta'' - L']-   \qquad (b)$$

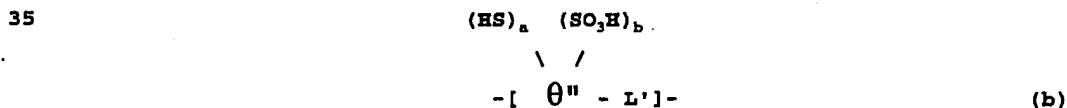wherein θ'' was an alkylene, arylene, cycloaliphatic, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were independently selected from integers from 1 to 20; L' was an optional linking group and - was a bond.

5   This invention further relates to novel catalytically-active polystyrene resins, characterized by bearing at least one of each of a mercapto-function and a sulfonic acid function on some individual styrene units of a polymer chain.

In yet another aspect, this invention relates to processes for
10   preparing the catalytically-active polystyrene resins. These processes preferably comprise steps of (b) sulfonating a haloalkylpolystyrene to produce an intermediate having sulfo functional groups; (c) optionally converting the sulfo functional groups to corresponding alkali metal salts; (d) thiolating the thus-produced sulfostyrene intermediate by
15   reacting the halo function with a reactive thiolate to produce a corresponding mercapto group or precursor thereof;(e) optionally hydrolyzing the thus-thiolated intermediate with an acid or base when the thiolated group so requires and (f) optionally acidifying (if so required) to produce sulfonic acid functional groups units.

20   The process of the invention permits use of very low levels of a single acidic condensing agent. The process permits simplified product isolation procedures, recycle procedures, and/or waste management. The process does not require a neutralization step to remove hydrochloric or sulfuric acid and does not produce a waste salt stream. The acidic
25   condensing agents used in the process of this invention were readily removed from the reaction mixtures and can be recovered and recycled.

The process of this invention results in high selectivity toward preferred bis-(4-hydroxyaryl) isomers and very fast reaction rates.

The process of this invention was particularly useful for the
30   preparation of bis(hydroxyaryl) compounds, such as bisphenol A and 9,9-bis-(4-hydroxyphenyl)fluorene, both of which were useful in the preparation of polycarbonates and other commercially significant polymers.

The heterogeneous catalysts disclosed herein advantageously were more reactive than heterogeneous catalysts currently used. They
35   advantageously allow using lower temperatures with correspondingly greater selectivity for desired product than was currently experienced. Greater selectivity reduces purification necessary to produce a desired or

preselected purity of product. Thus, for a commercially produced
bisphenol like bisphenol A, a heterogeneous catalyst disclosed herein can
be advantageously substituted in an existing commercial process, run with
the same or higher throughput at a lower temperature with less
5   purification to achieve at least equally pure product.

Ketones or aldehydes and phenolic compounds (hereinafter phenol,
phenols, a phenol or phenolic starting material) useful in process of the
invention were known in the art and were described in the literature, for
instance, Jansen '982, supra, Maki et al., '252, supra, Morgan '165,
10   supra, and Knebel et al., '594, supra.

The condensations of this invention can be represented by the
equation for a representative condensation, that of phenol with 9-
fluorenone:

15
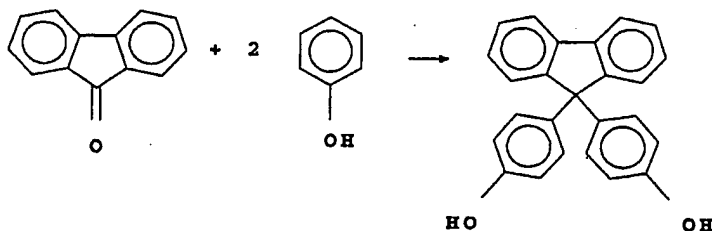
The process for making bisphenol A can be represented by the
equation:
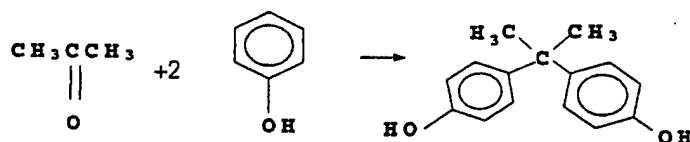
20   Phenol starting materials were advantageously any aromatic hydroxy
compounds which have at least one unsubstituted position, and optionally
have one or more inert substituents, such as hydrocarbyl or halogen at the
one or more ring positions. An inert substituent was a substituent which
does not interfere undesirably with the condensation of the phenol and
25   ketone or aldehyde and which was not, itself, catalytic. Preferably, the
phenols were unsubstituted in the position, para to the hydroxyl group.

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Alkylene (alk), alkyl, cycloaliphatic, aryl, arylene (ar), alkyl-
arylene (allkar), arylalkylene (aralk), alkylcycloaliphatic and alkylene-
cycloaliphatic were hydrocarbyl functions, that was, functions containing
carbon and hydrogen atoms. The alkylene functions can be straight-chain
5   or branched-chain and saturated or unsaturated, that was alkylene,
alkenylene, or alkynylene.   Cycloaliphatic hydrocarbon residues include
both saturated and unsaturated cyclic residues, that was, cycloalkylene
and cycloalkenylene. Arylene includes mono- and polycyclic aromatic
residues, for example, those of benzene, biphenyl, biaryl, naphthyl,
10   phenanthrenyl, anthracenyl or aryl groups, including those bridged by an
alkylene group. Alkaryl residues include alkyl, alkenyl and alkynyl-
substituted aromatic rings. Aralkyl includes alkyl, alkenyl or alkynyl
residues, substituted by one or more aromatic groups.

Alkyl groups include both straight-chain and branched-chain isomers
15   of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl,
decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl,
heptadecyl, nonadecyl and eicosyl groups, as well as the corresponding
unsaturated (alkenyl or alkynyl) groups, as well as higher homologues.
Preferably, the alkyl groups were of 1 to 20 carbon atoms, more preferably
20   of 1 to 5 carbon atoms, most preferably those of 1 to 3 carbon atoms.
Alkyl of 1 to 5 carbon atoms includes the various methyl, ethyl, propyl,
butyl and pentyl isomers.

Alkyl, aryl, alkaryl and aralkyl substituents were suitable
hydrocarbyl substituents on the phenol reactant.
25   Other inert substituents on the phenols include, but were not
limited to alkoxy, aryloxy or alkaryloxy, wherein alkoxy includes methoxy,
ethoxy, propyloxy, butoxy, pentoxy, hexoxy, heptoxy, octyloxy, nonyloxy,
decyloxy and polyoxyethylene, as well as higher homologues; aryloxy,
phenoxy, biphenoxy, naphthyloxy and alkaryloxy includes alkyl, alkenyl and
30   alkylnyl-substituted phenolics.

Additional inert substituents in phenols includes halo, such as
bromo, chloro or iodo.

Cyano and nitro substituents may deactivate the phenols and aldehyde
and carboxylic acid substituents may cause interfering reactions.
35   Additional hydroxyl substituents may be suitable in some cases.

Preferred substituents include alkyl moieties containing from 1 to
10 carbon atoms, more preferably, lower alkyl moieties, containing from 1

to 5 carbon atoms, most preferably from 1 to 3 carbon atoms. The alkyl substituents may be straight-chain or branched-chain isomers.

Exemplary phenols include, but were not limited to, phenol, 2-cresol, 3-cresol, 4-cresol, 2-chlorophenol, 3-chlorophenol, 4-chlorophe-

5   nol, 2-tert-butylphenol, 2,4-dimethylphenol, 2-ethyl-6-methylphenol, 2-bromophenol, 2-fluorophenol, 2-phenoxyphenol, 3-methoxyphenol, 2,3,6-trimethylphenol, 2,3,5,6-tetramethylphenol, 2,6-xylenol, 2,6-dichlorophenol, 3,5-diethylphenol, 2-benzylphenol, 2,6-di-tertbutylphenol, 2-phenylphenol, 1-naphthol, 2-naphthol. Preferred phenols include phenol,

10   2- or 3-cresol, 2,6-dimethylphenol, resorcinol, naphthols, and mixtures thereof. Most preferably, the phenol was unsubstituted.

The ketones which were advantageously used include any ketone having a single ketone carbonyl (C=O) group or several ketone carbonyl groups, and which were reactive under the conditions used. The ketones can be

15   substituted with substituents, which were inert under the conditions used. Inert substituents were as set forth above for the reactive phenols.

The ketones were advantageously selected from aliphatic, aromatic, alicyclic or mixed aromatic-aliphatic ketones, diketones or polyketones, of which acetone, methyl ethyl ketone, diethyl ketone, benzil,

20   acetylacetone, methyl isopropyl ketone, methyl isobutyl ketone, acetophenone, ethyl phenyl ketone, cyclohexanone, cyclopentanone, benzophenone, fluorenone, indanone, 3,3,5-trimethylcyclohexanone, anthraquinone, 4-hydroxyacetophenone, acenaphthenequinone, quinone, benzoylacetone and diacetyl were representative examples.

25   Ketones having halo, nitrile or nitro substituents can also be used; for example, 1,3-dichloroacetone or hexafluoroacetone.

Aliphatic ketones which were useful starting materials include, but were not limited to acetone, ethyl methyl ketone, isobutyl methyl ketone, 1,3-dichloroacetone, hexafluoroacetone. A preferred aliphatic ketone was

30   acetone, which condenses with phenol to produce 2,2-bis-(4-hydroxyphenyl)-propane, commonly known as bisphenol A. Another preferred aliphatic ketone was hexafluoroacetone, which reacts with two moles of phenol to produce 2,2-bis-(4-hydroxyphenyl)-hexafluoropropane (bisphenol AF).

A preferred class of ketones has at least one hydrocarbyl group

35   containing an aryl group, for example, a phenyl, tolyl, naphthyl, xylyl or 4-hydroxyphenyl group.

Other preferred ketones include those in which the hydrocarbon radicals connected to the carbonyl groups of the ketone was in a cycloaliphatic group. Examples of specific preferred ketones include 9-fluorenone, cyclohexanone, 3,3,5-trimethylcyclohexanone, indanone,

5   indenone, and anthraquinone.

Most preferred ketones include 9-fluorenone, benzophenone, acetone, acetophenone, 4-hydroxyacetophenone and 4,4'-dihydroxybenzophenone. Most preferably, the process of this invention was used to make bisphenol A by reaction of phenol with acetone or to make 9,9-bis-(4-

10   hydroxyphenyl)fluorene (BHPF) by reaction of phenol with 9-fluorenone.

The process of this invention can also be used for the condensation of phenols with aldehydes; for example, with formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde or higher homologues of the formula RCHO, wherein R was alkyl of 1 to 20 carbon atoms. The condensation of two

15   moles of phenol with one mole of formaldehyde produces bis-(4-hydroxyphenyl)methane, also known as Bisphenol F.

It will be understood that dialdehydes and ketoaldehdyes, for example, glyoxal, phenylglyoxal or pyruvic aldehyde, can also be used.

The products were generally geminal bisphenols, that was, compounds

20   having one or more single carbon atoms to which were attached nuclei of two phenolic moieties. This single carbon atom corresponds to the carbonyl carbon of the ketone or aldehyde reactant. In the case of starting materials, containing more than one aldehyde or ketone carbonyl, the product will contain more than one geminal bisphenolic moiety. For

25   example, the condensate from acetyl acetone and phenol was 2,2,4,4-tetrakis-(hydroxyphenyl)pentane and the condensate from benzoylacetone was 2,2,4,4-tetrakis-(hydroxyphenyl)-4-phenylbutane.

The mercaptosulfonic acid catalyst was any species, whether soluble or insoluble in the reaction mixture, containing at least one thiol (SH)

30   group and at least one sulfonic acid (SO$_3$H) group, including any group which can be converted to a sulfonic acid group under the reaction conditions used.

In the specification and claims, the soluble mercaptosulfonic acid moiety was represented by the formula

35                          $(HS)_a\text{-}\Theta\text{-}(SO_3H)_b$

wherein θ was an alkylene, cycloaliphatic, arylene, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue and each of "a" and "b" was independently an integer from 1 to 20.

5   "Soluble mercaptosulfonic acid," as used in the specification and claims, means a compound which has some solubility in the reaction mixture and which can be removed from the mixture, at the end of the reaction, by extraction, ion-exchange, precipitation, absorption.

     "Insoluble mercaptosulfonic acid," as used in the specification and claims, means a material, which was insoluble in the reaction mixture.
10   These materials were generally polymeric organic resins, or catalytically-active compounds, bonded to an inorganic support.

     When θ was alkylene, the alkylene can be of 2 to 20 carbon atoms, including straight and branched chain alkylene moieties, corresponding heterochain moieties and alkylene substituted with inert substituents.
15   Inert substituents include, for example, alkoxy, alkenyl, alkynyl, halo, nitro, aryl.

     Representative mercaptoalkanesulfonic acids include, but were not limited to, 2-mercaptoethanesulfonic acid, 3-mercaptopropanesulfonic acid, 4-mercaptobutanesulfonic acid, 4-mercaptopentanesulfonic acid, 3-mercapto-
20   2,2-dimethylpropanesulfonic acid, 2,3-dimercaptopropanesulfonic acid, mercaptopropane-2,3-disulfonic acid, 2-benzyl-4-mercaptobutanesulfonic acid, 5-mercaptopentanesulfonic acid. Most preferred among this group of catalysts were 3-mercaptopropanesulfonic acid and 4-mercaptobutanesulfonic acids.

25   The types of mercaptoalkanesulfonic acids which were useable were exemplified by the following compounds of Formula I:

Q
|
HS ∕∖∕∖∕∖ SO₃H   Formula I(a)

HS ∕∖ Y ∕∖ SO₃H   Formula I(b)
                    |
                    Q
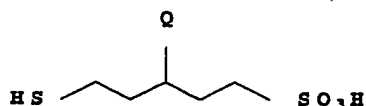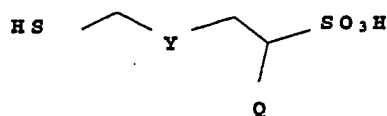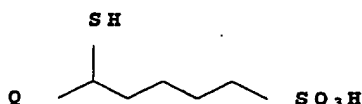
SH
|
Q ∕∖∕∖∕∖ SO₃H   Formula I(c)

wherein Q was an inert substituent and Y was an optional heteroelement,
for example O, N-Q or S. Q was H, hydrocarbyl, halo, carboxy, sulfonyl,
as described above for inert substituents on the phenol, ketone or
aldehyde starting materials. More than one Q may optionally be present.

5   The Q substituent can be at any position on the chain and more than one Q
can be present. As set forth in the general formula for the soluble
catalysts, more than one SH or sulfonic acid function were optionally
present in the catalyst.

Compounds of Formula I(a) are included within the generic formula

10                   $HS(CH_2)_yCH(Q)(CH_2)_zSO_3H$
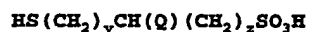
wherein y was an integer from 0 to 20, z was an integer from 0 to 20, Q
was an optional inert substituent and $y + z \geq 1$, up to a maximum of 40.

Compounds of Formula I(b) are included within the generic formula

                     $HS(CH_2)_y-Y-(CH_2)_zSO_3H$,
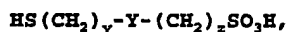
15   wherein one or more inert substituents, Q, can be attached at any point
along the carbon chain; wherein Y was a heteroelement, for example, -S-;
each of y and z was at least 1 and $y + z \geq 2$, up to a maximum of 40.
Preferred linear mercaptoalkanesulfonic acids were those in which the
distance between the mercapto and sulfonic acid functions were less than

20   20 atoms, including both carbon and heteroatoms. Compounds of Formula
I(b) can also have more than one SH and/or more than one sulfonic acid
function.

Compounds of Formula I(c) are included within the formula

$$\begin{array}{c} HS \\ | \\ CH(CH_2)_{y+z}SO_3H \\ | \\ Q \end{array}$$
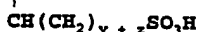
wherein y and z were as above.

Mercaptosulfonic acid precursors can also be used as catalysts, by conversion to active mercaptosulfonic acid catalysts in the reaction mixtures. For example, a precursor alkali metal sulfonate salt can be neutralized with a mineral acid to produce a free sulfonic acid. Sulfonate ester precursors can be hydrolyzed by treatment with a strong base, for example, sodium or potassium hydroxide, and thus converted to a corresponding alkali metal salt. A further precursor of sulfonic acids for the practice of this invention, was a sulfonyl halide group, which can readily converted to a corresponding sulfonic acid.

Mercaptosulfonic acids can be prepared from corresponding haloalkanesulfonic acids by reaction with an alkali metal mercaptide; for example,

$$X-alk-SO_3H + NaSH \rightarrow HS-alk-SO_3H + NaX$$
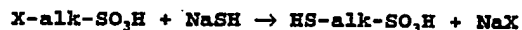
wherein X was Cl, Br or I and alk was alkylene, generally in accordance with Ellis et al., "The Preparation and Properties of a Double Series of Aliphatic Mercaptans," <u>J. Am. Chem. Soc.</u>, Volume 54 (1932), Pages 1674-1687.

Alternatively, treatment of a haloalkanesulfonic acid with an alkali metal thioacetate, followed by hydrolysis, can be used to prepare mercaptoalkanesulfonic acids.

Another route to mercaptosulfonic acids was by converting halides to a corresponding thiouronium salt, which was hydrolyzed with a strong base, as follows:

$$\begin{array}{c} X-alk-SO_3H + H_2NCSNH_2 \rightarrow HN=C-S-alk-SO_3H \\ | \\ NH_2 \cdot HX \end{array}$$

$$\downarrow NaOH$$

$$HS-alk-SO_3H$$
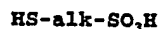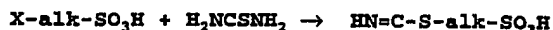
generally according to Schramm et al., "The Synthesis of mercaptoalkanesulfonic Acids," <u>J. Am. Chem. Soc.</u>, Volume 77 (1955), Pages 6231-6233.

-12-

Hydroxyalkanesulfonic acids can also be converted to the corresponding mercaptoalkanesulfonic acid by reaction with thiourea and HBr/HCl to produce a thiouronium salt, which was hydrolyzed using a strong base. See, Frank et al., "The Preparation of Mercaptans from Alcohols,"

5   J. Am. Chem. Soc., Volume 67 (1946), Pages 2103-2104.

Higher mercaptoalkanesulfonic acids can be prepared from higher olefinsulfonic acids, for example, oleyl sulfonic acid, by adding hydrogen sulfide across the olefinic bond. Alternatively, the olefinic bond of an olefinic sulfonic acid can be halogenated, for example, chlorinated, and

10 the halogen moiety replaced by a mercapto function, as above.

Mercaptoalkanesulfonic acids can also be made from corresponding sultones, for example, 1,4-butanesultone, in accordance with Chem. Abs., 90:86742m (1979); R. Fischer, "Propanesultone," Ind. Eng. Chem., Volume 56 (1964), Pages 41-45; or A. Mustafa, "The Chemistry of Sultones and

15 Sultams," Chemical Reviews, Volume 54 (1954), Pages 195-223.

When -θ- was arylene, the sulfonic acid and mercapto moieties were attached directly to an aromatic ring. Representative aromatic mercaptosulfonic acids include 2-mercaptobenzenesulfonic acid, 3-mercaptobenzenesulfonic acid, 4-mercaptobenzenesulfonic acid, 2-

20 mercaptonaphthalenesulfonic acid. The aromatic residues can be substituted with substituents, for example, H, alkyl, alkenyl, alkynyl, aryl, halo, alkoxy, aryloxy (Q, above), which were inert under the reaction conditions. The active catalysts can contain more than one SH and/or more than one sulfonic acid function in each molecule.

25 Cycloaliphatic residues include those of cyclohexane, cyclopentane and cycloheptane; the aliphatic ring of indane, Tetralin or benzocycloheptane. Representative cycloaliphatic mercaptosulfonic acids include, but were not limited to, 2-mercaptocyclohexanesulfonic acid, 2-mercaptocyclopentanesulfonic acid, 3-mercaptocyclohexanesulfonic acid, and

30 3-mercaptocyclopentanesulfonic acid. The cycloaliphatic rings can also be substituted with inert substituents and can contain more than one SH group and/or more than one sulfonic acid group.

Representative alkylenecycloaliphatic mercaptosulfonic acid compounds can be represented by the following formulas:

$C_zH_{2z}SO_3H$

$C_yH_{2y}SH$

$C_zH_{2z}SO_3H$

$C_yH_{2y}SH$

$C_zH_{2z}SO_3H$

$C_yH_{2y}SH$

Q

Q

Q

$Q - C_yH_{2y}SH$

$C_zH_{2z}SO_3H$
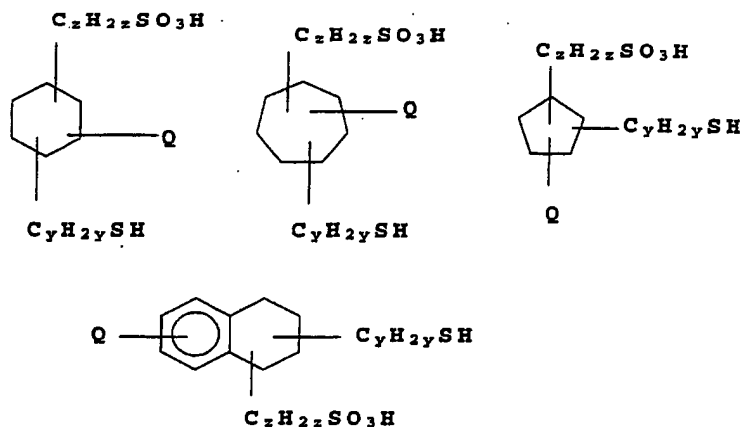
wherein y and z were integers of 0 to 20; Q was an optional inert substituent selected from alkyl, aryl, halo, alkoxy or aryloxy and $y + z \geq$ 1. Typical compounds include (mercaptomethyl)cyclohexanesulfonic acid and (mercaptomethyl)(sulfomethyl)cyclohexane.

5   Typical alkylenearyl mercaptosulfonic acids can be represented by the formulas:

Q

$HSC_yH_{2y} - C_zH_{2z}SO_3H$

Q

$C_yH_{2y}SH$

$C_zH_{2z}SO_3H$

Q

$C_zH_{2z}SO_3H$

$C_yH_{2y}SH$

$Q - C_yH_{2y}SH$

$C_zH_{2z}SO_3H$
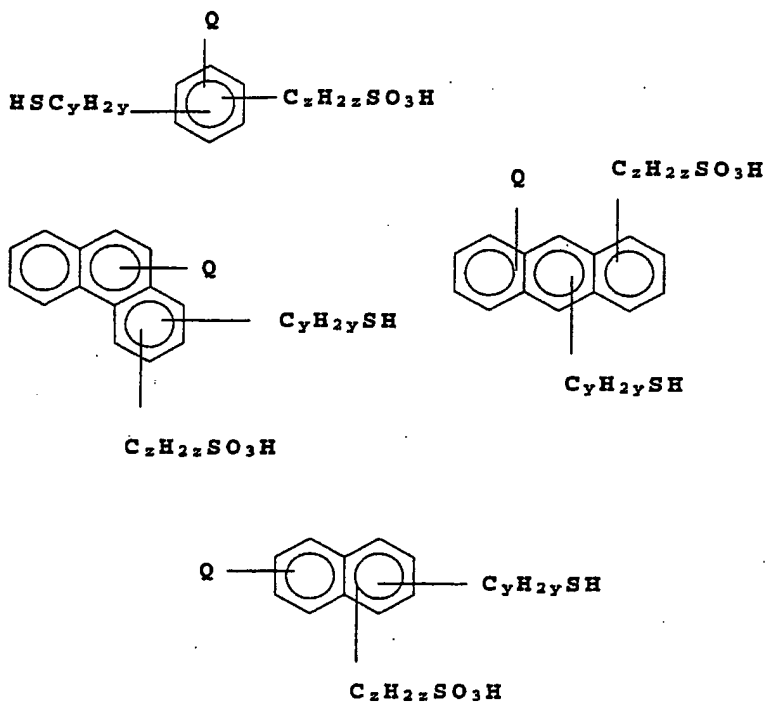
wherein x, y and Q were as above and x + y ≥ 1.

A typical compound of this group, (mercaptomethyl)benzene-sulfonic acid, can be prepared from a corresponding chloromethyl- or bromo-methylbenzenesulfonic acid.

5   Oligomers from vinylsulfonic acid can provide soluble materials, containing large numbers of mercapto and sulfonic acid groups. This type of soluble catalyst can be prepared from oligomers containing vinylsulfonic acid units, half of which can be converted to chlorosulfonyl units and reduced to mercapto units in accordance with the following

10   reaction scheme:

$$-[-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-]-$$
$$\begin{array}{cccc} | & | & | & | \\ SO_3H & SO_3H & SO_3H & SO_3H \end{array}$$

15   ↓

$$-[-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-]-$$
$$\begin{array}{cccc} | & | & | & | \\ SO_3H & SO_2Cl & SO_3H & SO_2Cl \end{array}$$

20   ↓

$$-[-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-]-$$
$$\begin{array}{cccc} | & | & | & | \\ SO_3H & SH & SO_3H & SH \end{array}$$
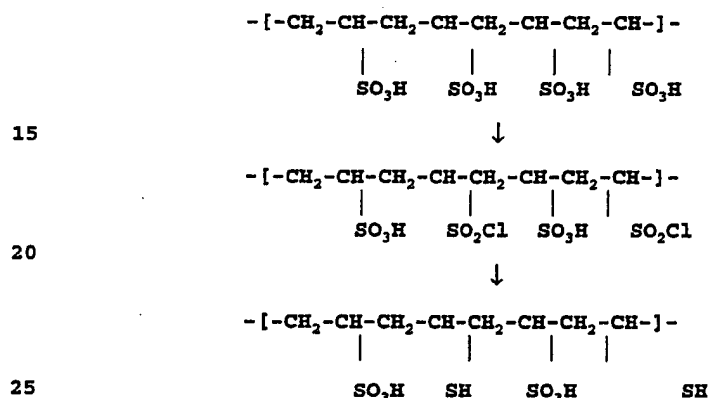
25   Another type of oligomeric catalysts, containing a multiplicity of mercapto and sulfonic acid units, can be prepared from propenesultone. Propenesultone was prepared as described by G. Manecke et al., _Chem. Abs._ 53:2083c (1959), Helberger et al., DE 1,146,870 and _Chem. Abs._ 59:11259

30   (1963). The sultone ring of the polymer can be opened, generally as above, to furnish mercaptosulfonic acid oligomers, containing a plurality of mercapto and sulfonic acid units.

In addition, oligomers containing a plurality of mercaptosulfonic acid functions can be prepared from oligomers of 4-allyl-1,4-

35   butanesultone. The monomer was prepared as described for 4-benzyl-1,4-butanesultone, using allyl chloride instead of benzyl chloride. 4,4-Diallyl-1,4-butanesultone can be prepared by addition of a second allyl group.

Other catalytically active mercaptosulfonic acid oligomers can be

40   prepared from allyl vinylsulfonate (CH=CHSO_2OCH_2CH=CH_2), which was polymer-ized to form a corresponding sultone-containing polymer in accordance with E. Goethals, "Synthesis and Polymerization of Allyl Vinyl Sulfonate,"

Polymer Letters, Volume 4 (1966), Pages 691-693. The resulting polymer, containing sultone groups was treated with a reactive thiolate to open the sultone rings and produce mercaptoalkyl sulfonate polymers.

The conversions can be represented by the equation:
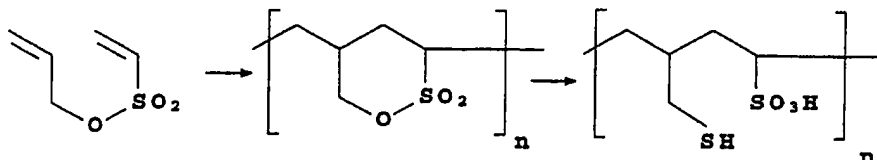
Similar catalytically-active solid oligomers can be prepared from oligomers of allyl allylsulfonate ($CH_2=CHCH_2SO_2OCH_2CH=CH_2$), which can be polymerized in accordance with E. Goethals et al., "Polymerization and Copolymerization of Allyl Sulfonate," _J. Macromol. Sci. - Chem._, Volume A5 (1971), Pages 63-72. The oligomers were converted to mercaptosulfonic acid functional materials by a corresponding ring opening reaction.

The conversion can be represented by the equation:
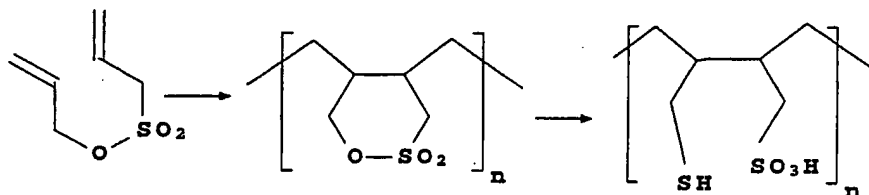
Heterocyclic residues advantageously include cyclic residues, containing N, O, or S. These will generally correspond to aromatic compounds, for example, residues from pyridine, thiophene, quinoline, phenanthridine, as well as the corresponding partially or fully hydrogenated compounds. Alkyleneheterocyclic residues otherwise correspond to aromatic residues of the same configuration, as do alkyl heterocyclic residues, as well as corresponding fully or partially hydrogenated compounds.

Preferred soluble mercaptosulfonic acids were compounds in which the mercaptan and sulfonic acid functions were separated by a chain of 2 to 10 atoms, whether the chain or linker arm was in an alkylene group or incorporated in an aromatic, cycloaliphatic or heterocyclic ring, whether or not the chain includes heteroelement, and whether or not the mercapto

and sulfonic acid functions were attached directly or indirectly to the ring structures. Preferred soluble catalysts for the practice of this invention were mercaptosulfonic acids in which a and b were independently from 1 to 4. More preferably, a and b were independently 1 or 2. Most preferred were mercaptosulfonic acids, containing mercapto and sulfonic acid functions in a 1:1 molar ratio, that was a and b were each 1, more particularly 3-mercaptopropanesulfonic acid and 4-mercaptobutanesulfonic acid.

When the mercaptosulfonic acid was insoluble, the heterogeneous catalyst comprises a catalytically-active species represented by Formula II:

$$(HS)_a\text{-}\theta'\text{-}(SO_3H)_b \qquad \text{Formula II}$$
$$|$$
$$L$$
$$|$$

in which each of a and b was independently an integer from 1 to 20, θ' was an alkylene, cycloaliphatic, arylene, alkylenearylene, alkylene-cycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue, L was an optional linking group and - was a bond, which catalytically-active species was attached by the bond - to an insoluble organic or inorganic support; or a catalytically-active species represented by Formula III:

$$(HS)_a \quad (SO_3H)_b \qquad (\text{Formula III})$$
$$\backslash \quad /$$
$$\text{-[} \theta'' - L' \text{]-}$$
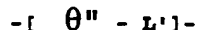
wherein θ'' was an alkylene, arylene, cycloaliphatic, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were independently selected from integers from 1 to 20; L' was an optional linking group and - was a bond.

Catalytically-active materials of Formula II were generally derived from polymers of ethylenic monomers, wherein the insoluble organic support was the main chain of a resulting polymer and -L- was a covalent bond or a linking group. This type of polymer will include unit structures represented by the general formula:

$$\text{-[CH}_2\text{CH]-}$$
$$|$$
$$L$$
$$|$$
$$(HS)_a\text{-}\theta'\text{-}(SO_3H)_b.$$

-17-
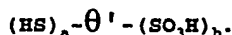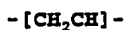
Preferably, the catalytically-active materials will include those
having from 1 to 4 of each of mercapto and sulfonic acid groups per θ'.
More preferably, the catalytically-active materials will include those
having 1 or 2 of each of mercapto and sulfonic acid groups per θ'. Most
5   preferably, the catalytically-active materials contain 1:1 ratios of
mercapto and sulfonic acid functions and will correspond to the general
formula:

$$-[CH_2CH]-$$

10
$$\mid$$
$$L$$
$$\mid$$
$$HS-\theta'-SO_3H.$$

Exemplary polymers, made from ethylenically unsaturated monomers and
which can be used as carriers for the catalytically-active species,
15   include, but were not limited to:

L	θ'	Monomer(s)
–	phenyl	styrene
-CH₂-	phenyl	allylbenzene
-O-	phenyl	phenyl vinyl ether
-COO-	alkyl, aryl	acrylic esters
-OCO-	alkyl, aryl	vinyl esters
-(CH₂)ᵣ- r = 4-20	alkenyl	α,ω-diolefins
-NH-	alkyl, aryl	vinylamines
-CONH-	alkyl, aryl	acrylamides
-NHCOO-	alkyl, aryl	vinylurethanes
–	alkylphenyl	vinyltoluene
–	phenyl	α-methylstyrene
-S-	phenyl	phenyl vinyl ether
-SO₂-	aryl	vinyl aryl sulfones
-SO-	aryl	vinyl aryl sulfoxides
-NSO₂-	aryl	aryl sulfonamide

The linking groups, -L-, accordingly can include alkylene, a
covalent bond, oxycarbonyl, carbonyloxy, oxy, ureido, amido, amino, thio
20   (sulfur), sulfono or sulfoxo. Preferred linking groups include a covalent

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bond, methylene, sulfur or oxygen, more particularly a covalent bond
joining a phenyl ring to a carbon backbone in polystyrene or polystyrene
derivatives, each containing SH and SO_3H functions in single monomeric
units of polystyrene.

5   One type of novel catalytically-active polystyrene resins, includes
unit structures represented by Formula IV:

$$\text{Formula} \qquad \begin{array}{c} B \\ | \\ CRSO_3H \\ | \\ C_nH_{2n} \qquad IV \\ | \\ CHR^1SH \end{array}$$

20
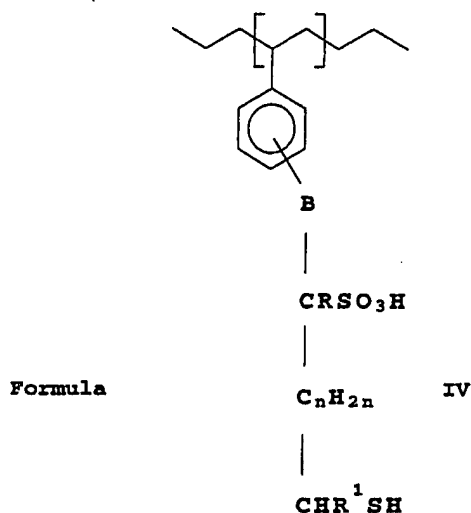
wherein B was a bridging group, R and R^1 were independently selected from
H, alkyl or aryl, $-C_nH_{2n}-$ was straight or branched chain alkylene and n was
an integer from 0 to 20.

        The bridging group B, can be selected from alkylene, generally as
25   above. Alkyl and aryl are defined above.

        Polystyrene resins of Formula IV can be made by the steps of (a)
reacting a haloalkystyrene polymer with a lithiated sultone, (b) treating
a resulting sultone-functionalized polymer with a reactive thiolate and
(c) acidifying the resulting intermediate to produce a polymer containing
30   (mercaptosulfoalkyl)styrene units.

        Haloalkylstyrene polymers include, but were not limited to
poly(chloromethylstyrene), poly(bromomethylstyrene),
poly(bromopropylstyrene), poly(bromopentyl)styrene.
Including homopolymers and copolymers, whether made by polymerization of
35   haloalkylstyrene monomers or haloalkylation of polystyrene resins.
Representative starting materials can be made by copolymerization of
vinylbenzyl chloride or vinylbenzyl bromide with styrene. Either starting

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material can be crosslinked with divinylbenzene or similar crosslinking monomers. The polymers can contain other monomers, for example, styrene, α-methylstyrene, acrylonitrile, butadiene, maleic anhydride, ethylene or propylene.

5 ·   The haloalkylated polymers will advantageously contain from 0.5 meq/g to 10 meq/g of halomethyl groups. Halomethylated or haloalkylated polymers normally comprise mixtures of polymers, substituted in the ortho, meta- and para-positions.

      Poly(chloromethylstyrene), containing 2 to 5 meq/g of chlorine, was

10   a preferred starting material.

      The reaction sequence described above can be performed utilizing a variety of chloromethylated or bromomethylated styrene polymers or copolymers. In particular, crosslinked halomethylated styrene/divinylbenzene copolymers in various forms, for example,

15 microporous or macroporous beads, powders, can be functionalized to provide the corresponding mercaptosulfonic acid polymers.

      In the case of all the polymer-based catalysts utilization of the functionalized styrene or other polymers in bead form may advantageously simplify workup procedures during preparation and provide for more facile

20 implementation in catalyst applications. Beads were suitably of any size through which effective flow and contact was achieved. Physical forms including powders, beads, extruded shapes, macroporous and microporous configuration were; however, suitably used in the practice of the invention. In general smaller size provides more surface area for

25 contact, but larger size permits greater flow through a bed. Optimizing these factors was within the skill of the art.

      Reactive thiolates advantageously include, but were not limited to, sodium thioacetate, potassium thioacetate, ammonium thioacetate and lithium thioacetate and the corresponding hydrosulfides. Of these,

30 lithium, sodium or potassium thioacetate was preferred.

      When conversion to a mercapto function was done through a thiourea intermediate, the thioureas were advantageously selected from thiourea, N-methylthiourea, N-ethylthiourea, N-phenylthiourea. In another alternative procedure, sodium thiosulfate can be used.

35   A preferred species of catalytically-active polystyrene resin was made by reacting poly(chloromethyl)styrene with lithiated 1,4-

butanesultone to produce an intermediate sultone, represented by the
structural unit formula:

$$
\begin{array}{c}
\text{CH}_2 \\
| \\
\text{CHSO}_2\text{O} \\
| \qquad \backslash \\
(\text{CH}_2)_2\text{CH}_2
\end{array}
$$
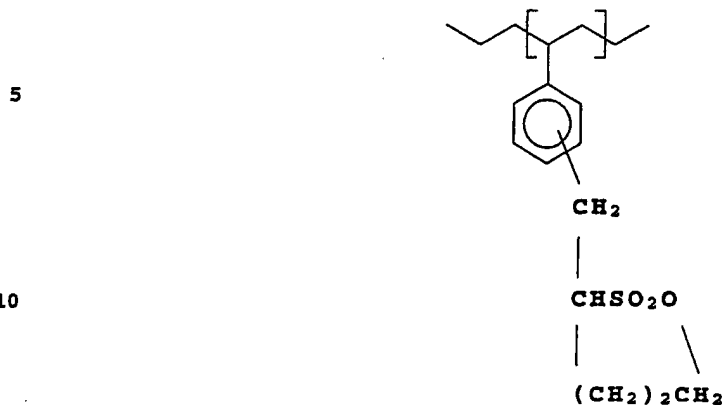
The resulting polymer contained (ε-mercapto-β--sulfopentyl)styrene
units, that was, n in Formula IV was 2 and B was -CH$_2$-.

Most preferably, this type of resin was made from a slightly
crosslinked polystyrene; the resulting catalytically active material was
designated as PMBSA-MER.

Another type of catalytically-active polystyrene resins can be
prepared by the steps of:

(a)   alkylating a polystyrene with an alkenyl halide of the formula
RC(R^1)=C(R^2)C$_m$H$_{2m}$CH(R^3)X, wherein each of R, R^1, R^2 and R^3 was H, alkyl or
aryl; m was 0 to 20 and X was F, Cl, Br or I to produce a haloalkyl
polystyrene;

(b)   sulfonating the resulting haloalkylpolystyrene to produce an
intermediate having sulfo-functional groups;

(c)   optionally converting the sulfo-functional groups to a sodium
or potassium sulfonate function;

(d)   thiolating the thus-produced sulfostyrene intermediate by
reacting the halo function with a reactive thiolate to produce a
corresponding mercapto function or precursor thereof, and

(e)   optionally hydrolyzing the thus-thiolated intermediate with an
acid or base when the thiolated group so requires; and

(f)   optionally acidifying (if so required) to produce the sulfonic
acid function.

This process can be represented broadly by the reaction sequence:

$+ R(R^1)C=C(R^2)C_mH_{2m}CH(R^3)X$

or

$R-C-R^1$

$H-C(R^2)$

$C_mH_{2m}CH(R^3)X$

$R_2-C-CR(R^1)H$

$C_mH_{2m}CH(R^3)X$

sulfonation

$-SO_3H$

$R-C-R^1$

$C(R^2)H$

$C_mH_{2m}CH(R^3)X$

or

$-SO_3H$

$R^2-C-CR(R^1)H$

$C_mH_{2m}CH(R^3)X$

-22-
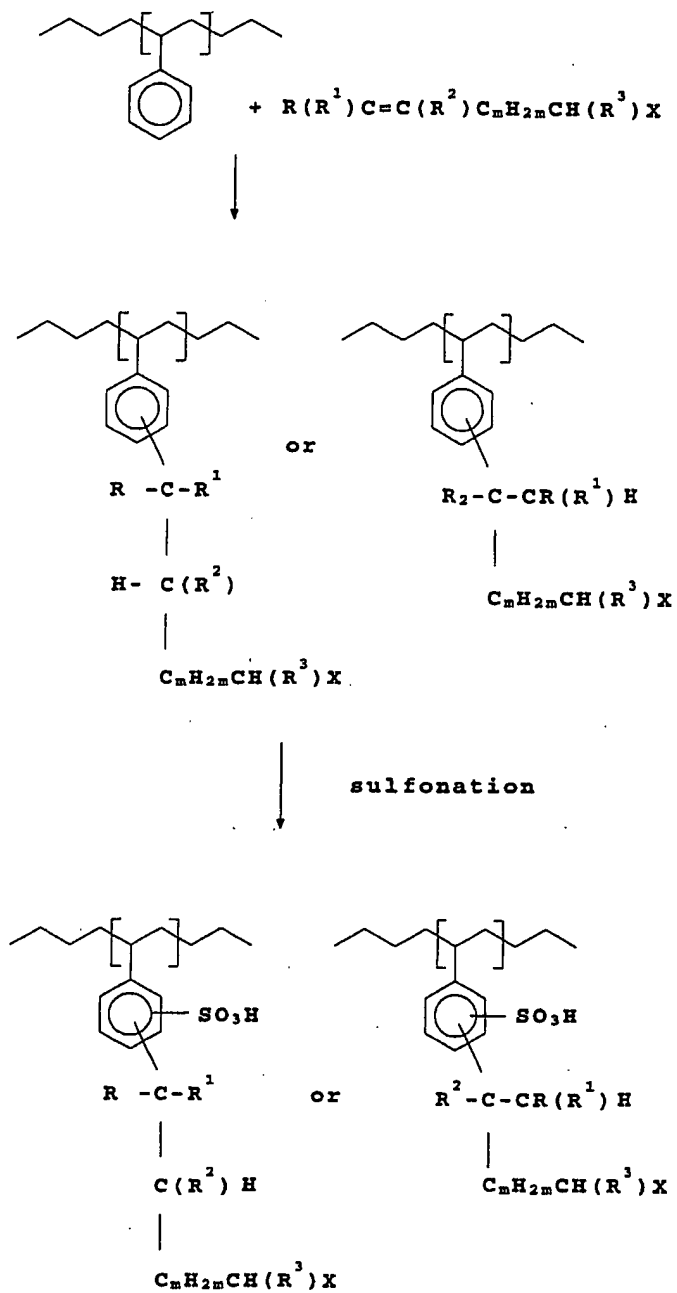
to produce intermediate haloalkyl sulfonated styrene polymers, of which halo functions were converted to mercapto-functions to produce the following types of products of Formula V:

$$HO_3S \quad R-C-R^1 \qquad SO_3H \qquad R^2-C-CR(R^1)H$$

$$C(R^2)H \qquad\qquad\qquad C_mH_{2m}CH(R^3)SH$$

$$C_mH_{2m}CH(R^3)SH$$

with SO_3H shown on third ring.
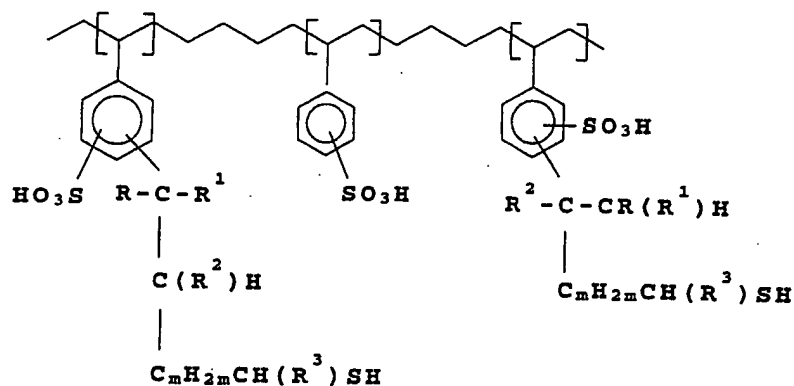
5   Alkenyl halides optionally contain aryl and alkyl substituents, as defined above. Representative alkenyl halides, useful for preparing the catalytically-active polymers, include, but were not limited to, allyl chloride, allyl bromide, allyl iodide, methallyl chloride, methallyl bromide, crotyl chloride, crotyl bromide, 4-bromo-1-butene, 5-bromo-1-

10   butene, 6-bromo-1-hexene or higher chloro or bromoalkenes. Preferably, the alkenyl halides were allylic halides, represented by the formula $RC(R^1)=C(R^2)CH(R^3)X$. Most preferably, the alkenyl halide was 5-bromo-1-pentene, 11-bromo-1-undecene or allyl bromide.

A particularly preferred product thus made can be characterized by

15   the formula, in the case of a product from 5-bromo-1-pentene:
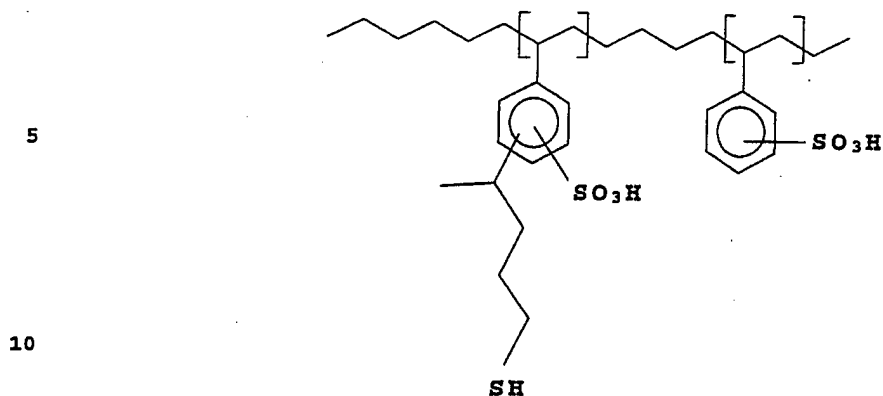
or, when the halide was allyl bromide or allyl chloride, by the formula:
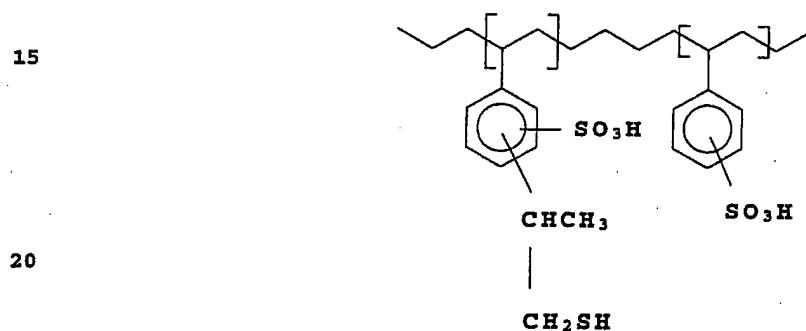
Reactive thiolates were as defined above. Most preferably, the reactive thiolate was an alkali metal thioacetate or hydrosulfide.

By varying the choice of starting bromoalkene (or other haloalkene) used in the alkylation step of the process, the basic procedure described above can also be used to prepare a variety of catalysts with varying chain lengths between the mercaptan and sulfonic acid moieties. A number of catalysts with different amounts of mercaptosulfonic acid sites, depending upon the degree of functionalization in the alkylation and sulfonation steps in the process, and structural relationships between the mercaptan and sulfonic acid sites, depending upon the choice of bromo- or chloroalkylating agent, can accordingly be made.

Preferred catalytically-active species of Formula V were those derived from polystyrenes, treated with 5-bromo-1-pentene, 11-bromo-1-undecene or an allylic halide of the formula $RCH=CH_2CH_2X$, wherein R was H or alkyl of 1 to 5 carbon atoms.

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In another aspect, this invention relates to novel
(mercaptoalkyl)(sulfo)phenylalkyl sulfonated polystyrene catalysts, made
by a process comprising the steps of:

    (a) alkylating a haloalkylated polystyrene with a haloalkylarylene
5   compound to produce an intermediate haloalkylpolystyrene having
(haloalkyl)phenylalkyl styrene units;

    (b) sulfonating the thus-produced haloalkylpolystyrene
intermediate to produce an intermediate having sulfo-functional groups;

    (c) optionally converting the sulfo functional groups to
10   corresponding alkali metal salts;

    (d) thiolating the thus-produced sulfostyrene intermediate by
reacting the halo function with a reactive thiolate to produce a
corresponding mercapto function or precursor thereof and

    (e) optionally hydrolyzing the thus-thiolated intermediate with an
15   acid or base when the thiolated group so requires; and

    (f) optionally acidifying (if so required) to produce the sulfonic
acid function.

This process produces polymers having repeating units of the
formula:

20
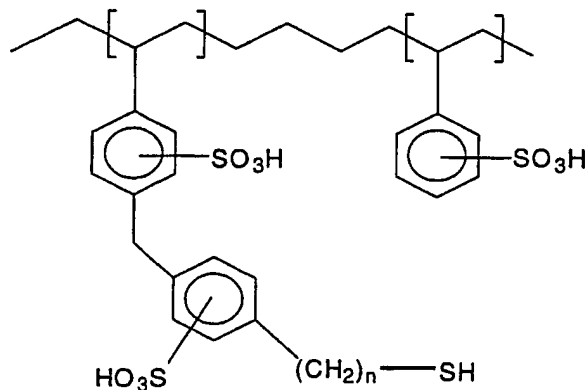
wherein n was preferably an integer from 0 to 10, more preferably 2 or 3.

A representative member of this series of polymers, designated as
DPMSA-XE3C was made from chloromethylstyrene polymer and 3-
25   bromopropylbenzene, in accordance with the following reaction sequence:

alkylation

Lewis acid

sulfonation

1) ClSO₃H

2) NaHCO₃

thiolation

1)   Na thioacetate

2)   acid hydrolysis
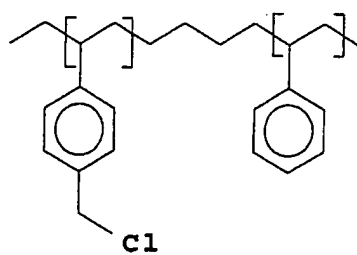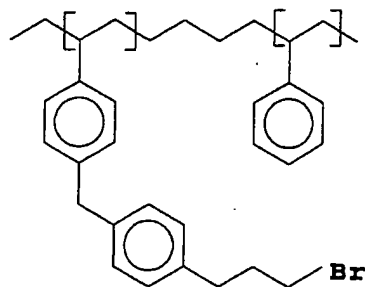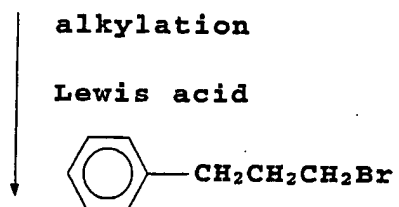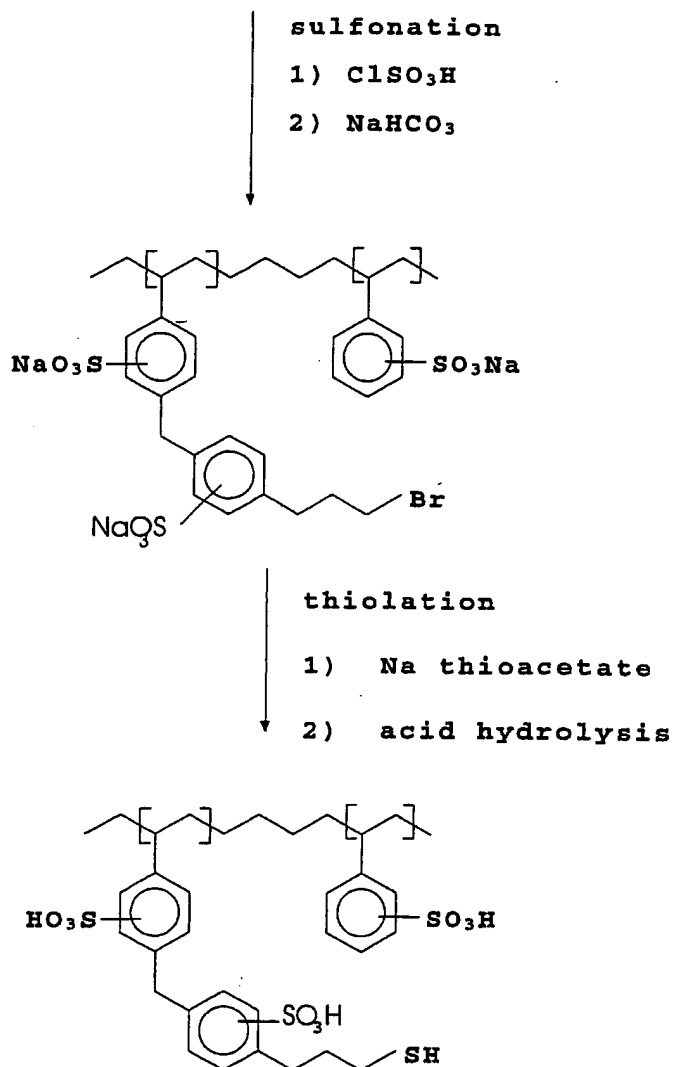
The haloalkyl polystyrene starting materials can advantageously be
selected from chloromethylated polystyrenes, bromomethylated polystyrenes,
chloroethylated polystyrenes, iodoethylated polystyrenes, generally as
above, preferably the halomethylated polystyrenes. Those skilled in the
art recognize that selectivity decreases with haloalkyl groups on aryl
rings which groups have similar selectivity.

The haloalkylaryene compound can conveniently be selected from
chlorobenzene, (chloromethyl)benzene, (chloroethyl)benzene,
(chloropropyl)benzene, (chlorobutyl)benzene, as well as the corresponding
fluoro, bromo and iodo analogues. Representative examples include (2-

chloroethyl)benzene, (2-bromoethyl)benzene, (2-iodoethyl)benzene, 1-
chloro-3-phenylpropane, 1-bromo-3-phenylpropane, and 1-iodo-3-
phenylpropane. The bromo compounds were preferred.

　　　　The alkylation was conveniently carried out in the presence of a
5   Friedel-Crafts catalyst, of which aluminum trichloride, aluminum bromide,
boron trifluoride, hydrogen fluoride, phosphoric acid, zinc chloride,
titanium chloride, ethylaluminum dichloride and stannic chloride were
representative. A preferred catalyst was aluminum chloride in
nitromethane or nitrobenzene, as disclosed by A. Warshawsky et al.,
10   "Functionalization of Polystyrene. I. Alkylation with Substituted Benzyl
Halide and Benzyl Alcohol Compounds", J. Org. Chem., Volume 43 (1978),
Pages 3151-3157.

　　　　Conveniently, after alkylation, unreacted haloalkylbenzene, solvent
and catalyst in the admixture were removed from the alkylated polystyrene
15   by means within the art such as filtration. Advantageously, the admixture
was recycled for reaction with additional haloalkyl polystyrene. The
alkylated polystyrene was optionally washed with a solvent such as
dichloromethane and optionally dried.

　　　　The resulting alkylated polystyrene was sulfonated using
20   chlorosulfonic acid, oleum or other known sulfonating agents. Prior to
conversion of the halo moiety to the mercapto moiety, it was convenient to
convert the sulfo moieties to corresponding alkali metal salts.
Chlorosulfonic acid, sulfuric acid or sulfur trioxide was conveniently
used in an amount sufficient to achieve a predetermiend or desirable
25   degree of sulfonation, advantageoulsy to avoid unnecessary workup, in an
amount not in large excess of the sufficient amount which varies with each
resin but was determined without undue experimentation. The advantages of
lower reaction temperatures were greater with chlorosulfonic acid.

　　　　The thiolating reagents were conveniently selected from those
30   disclosed above. Sodium thioacetate was preferred. Excess sodium
hydrosulfide was optionally used for thiolation. Hydrolysis was then
unnecessary since a thio group rather than a thioacetate was formed. The
intermediate thiolated compound was, if necessary, acidified with a strong
acid to convert sulfonate salt moieties to corresponding sulfonic acid
35   moieties. Advantageously, a mineral acid was used, as above.

　　　　In an alternate embodiment, the process comprises:

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(a)   alkylating a polystyrene resin with a halomethyl haloalkylarylene compound to produce an intermediate having (haloalkyl)phenylalkyl styrene units;

(b)   sulfonating the thus-produced intermediate to produce an intermediate having sulfo-functional groups;

(c)   optionally converting the sulfo functions to corresponding alkali metal salts;

(d)   thiolating the thus-produced sulfostyrene intermediate by reacting the halo function with a reactive thiolate to produce a corresponding mercapto function or precursor thereof and

(e)   optionally hydrolyzing the thus-thiolated intermediate with an acid or base when the thiolated group so required; and

(f)   optionally acidifying (if so required) to produce the sulfonic acid function.

Illustrative of this reaction was the following sequence:
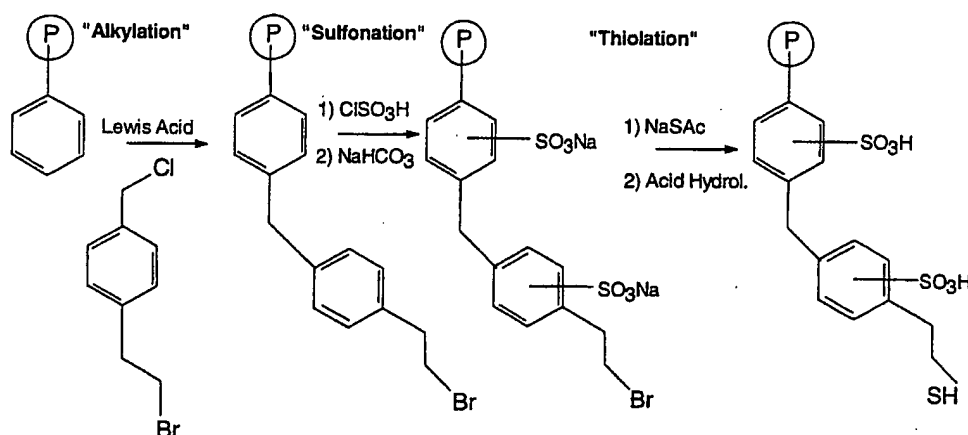
The alkylating step was performed as in the preceding process optionally in a solvent such as chloroform, 1,2-dichloroethane, dichloromethane, 1,2-dichloropropane, preferably a solvent which swells polystyrene (for example, styrene/divinylbenzene copolymer beads). The alkylating agent was any halomethyl haloalkylarylene preferably wherein the alkyl group has from 0 to 10 carbon atoms. The arylene group preferably has from 6 to 14 carbon atoms.

It was within the skill of the art to select halomethyl haloalkylarylenes in which the haloalkyl and halomethyl groups have activities sufficiently different to achieve the desired result.

Representative halomethyl haloalkylarylene compounds include
(2-bromoethyl)benzylchloride and (3-bromopropyl)benzylchloride. Chloromethyl haloalkylarlenes were conveniently prepared by means within the skill of the art such as described by Selva et al., Synthesis, 1991, 1003-1004, wherein haloalkylarylenes were reacted with formaldehyde in acid (for example, sulfuric or hydrochloric) in the presence of a quaternary ammonium phase transfer catalyst. Chloromethylation can also be performed using zinc chloride and paraformaldehyde in accordance with the method described by Daren in U.S. Patent No. 4,967,026. Alternatively, chloromethyl ethers were used to chloromethylate a haloalkyl arylene by methods similar to that taught by Raley in U.S. Patent No. 3,311,602, by Shinka, et al., J. Poly. Sci. Polym. Lett. Ed. 14(1), 1-3 (1976), and by Shigeo, et al., Chem. Abstr. 72:32290 (1970), or by other means within the skill of the art.

In another aspect, hydrohalogenating agents, such as, HBr were added to alkenyl arylenes, such as, styrene under radical forming conditions such as taught by Martan in U.S. Patent No. 4,228,106 or Plesmid in U.S. Patent No. 3,321,536. In an extension of these works, vinylbenzyl chloride was hydrobrominated by this method.

The sulfonation and thiolation steps were as described for the previous process.

In addition to the methods disclosed above, a variety of other methods were also available for preparing the haloalkyl-functionalized polystyrene resins which were precursors to the mercaptosulfonic acid polymer catalysts. Representative approaches for preparing the haloalkylated polystyrene resins include (but were not limited to) those described or discussed by: a) P. C. Reeves and M. S. Chiles, "Phase Transfer Catalysts Anchored to Polystyrene," Tetrahedron Letters (1979), Pages 3367-3370; b) M. Tomoi, et. al., "Novel Synthesis of Spacer-Modified Polymer Supports and Activity of Phase-Transfer Catalysts Derived from the Polymer Supports," J. Polymer. Sci. Polymer Chem. Ed., Volume 20 (1982), Pages 3015-3019; c) M. J. Farrall and J. M. J. Fréchet, "Bromination and Lithiation: Two Important Steps in the Functionalization of Polystyrene Resins", J. Org. Chem., Volume 41 (1976), Pages 3877-3882;

d) S. P. McManus and R. D. Olinger, "Reactions of Cyclic Halonium Ions and Alkylene Dihalides with Polystyryllithium. Preparation of Haloalkylated Polystyrene", J. Org. Chem., Volume 45 (1980), Pages 2717-2719; e) M. Haratake, et. al. "Sorption of Phenols on Anion-Exchange Resins Having

5   .omega.-Oxoalkyl or .omega.-Hydroxyalkyl Spacer," Analytical Sciences, Volume 4 (1988), Pages 591-594; f) M. Gauthier and A. Eisenberg, "Alkylated Styrene Ionomers with Variable Length Spacers. I. Synthesis," J. Polymer Sci.: Part A: Polymer Chem., Volume 28 (1990), Pages 1549-1568; g) P. Tundo, "Easy and Economical Synthesis of Widely Porous Resins; Very

10   Efficient Supports for Immobilized Phase-Transfer Catalysts," Synthesis (1978), Pages 315-316; h) Tachikawa, et al., "Process for the Production of Silanes", (U. S. Patent No. 4,725,420); i) G. Zheng, et al., "Synthesis of Bromoalkylated Crosslinked Polystyrene", Xinan Shifan Daxue Xuebao, Ziran Kexueban, Volume 2 (1986) Pages 68-70; j) M. L. Hallensleben,

15   "Preparation of Poly(p-(.omega.-lithiumalkyl)styrenes) and Their Use as Polymer Metalating Agents", Angew. Makromol. Chem., Volume 31 (1973), Pages 147-159; k) F. Döscher et al., "Synthesis of Sulfoalkylated Styrene-Divinylbenzene Copolymers", Makromol. Chem., Rapid Commun., Volume 1 (1980), Pages 297-302.

20   It was to be understood that a haloalkylated polystyrene resin prepared in a manner such as that described in the above references could be further functionalized by the sulfonation and thiolation procedures previously described to provide a mercaptosulfonic acid polymer catalyst.

            Other representative references on methods for polymer modification
25   or for uses of functional polymers include Akelah et al., "Application of Functionalized Polymers in Organic Synthesis", Chem. Rev., Volume 81 (1981), Pages 557-587; Fréchet et al., "Functionalization of Crosslinked Polystyrene Resins by Chemical Modification: A Review in "Chemistry and Properties of Crosslinked Polymers", S. Labana, ed., Academic Press, New

30   York (1977), Pages 59-83; and Maréchal, "Chemical Modification of Synthetic Polymers", in "Comprehensive Polymer Science", Volume 6, Allen, ed., Pergamon Press, New York, Pages 1-47.

            Catalysts derived from polystyrenes will advantageously contain from 0.2 to 5 meq of mercaptosulfonic acid functionality per g, most preferably
35   from 2 to 4 meq/g.

            It will be understood that polymers, containing large amounts of mercaptosulfonic acid functionality on a given carrier, pendant from a

hydrocarbon chain, can be prepared by grafting vinylsulfonic acid, propenesultone, to the pendant carrier function, and converting the grafted polymer to materials having mercapto/sulfonic acid functionality.

Catalytically-active polymers in which - was an ionic bond can advantageously be prepared from ion-exchange resins and reactive compounds, containing both mercapto and sulfonic acid functions.

For example, a strongly basic ion-exchange resin such as poly(vinylbenzyl amine) can be reacted with a compound such as 4-mercapto-1,2-butanesulfonic acid to produce catalytically-active material as represented by the equation:

$$\sim\!\!\!\wedge\!\!\!\wedge\!\!\left[\!\!\!\wedge\!\!\right]\!\!\wedge\!\!\!\wedge\!\!\sim$$

$$C_6H_4\!\!-\!\!CH_2NH_2$$

$$\downarrow HSCH_2CH_2CH(SO_3H)CH_2SO_3H$$

$$CH_2NH_3^+\ ^-O_3SCH_2CH(SO_3H)CH_2CH_2SH$$
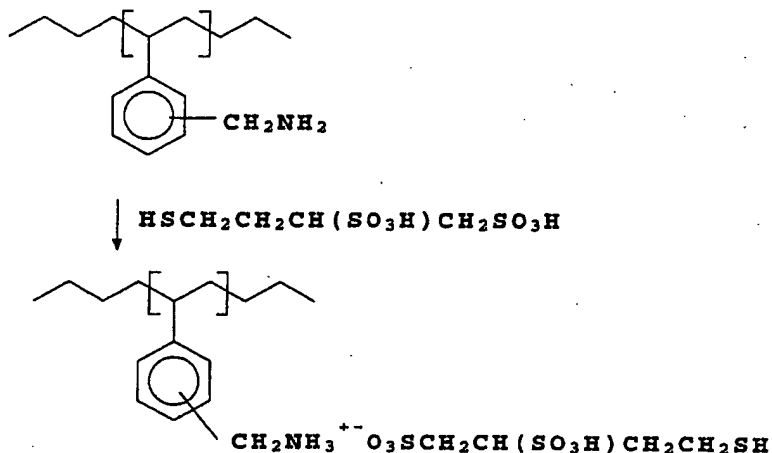
Representative strongly basic ion-exchange resins include DOWEX™ 1X2-400, from The Dow Chemical Company, Amberlyst™ A-21 from Rohm and Haas, DOWEX™ WGR-1, DOWEX™ WGR-2 and DOWEX™ MSA-1, from The Dow Chemical Company. The WGR resins were polypropyleneimines, conveniently obtained by condensation of epichlorohydrin with ammonia.

Catalytically-active materials can also advantageously be prepared from an acidic ion-exchange resin, for example sulfonated polystyrene by reaction with an aminomercaptosulfonic acid, for example, 2-mercapto-4-aminobenzene sulfonic acid, as represented by the equation:

5

10

15
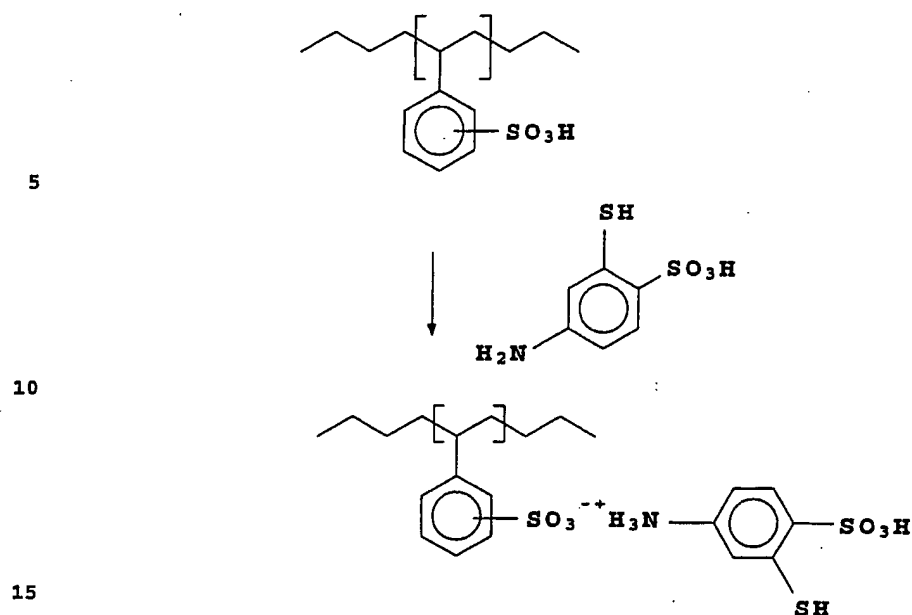
Representative strongly acidic cation-exchange resins include DOWEX™
50X2-400, Amberlyst™ A-21, from Rohm and Haas, and DOWEX™ MSC-1, from The
Dow Chemical Company.

20   In addition to the use of polymers from ethylenically unsaturated
monomers, including copolymers, as insoluble supports for the
catalytically-active species, the catalytically-active species can be
attached to an inorganic support, for example a mineral, such as silica,
alumina, aluminosilicates or glass, through the linking group -L-. A
25 representative case was that wherein the linking group was -OSiO- or

$$-O-P(=O)-O-,$$
$$|$$
$$O$$
$$|$$
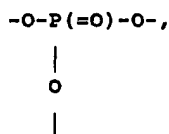
30

most preferably, -OSiO-.

Catalytically-active species of Formula III will conveniently be
incorporated in the backbone of condensation polymers; for example,
polyesters, polyamides, polycarbonates, polyurethanes, polysiloxanes,
35 polyamines, polyethers, polyketones, polysulfones and polysulfoxides. The
divalent linking group, -L'-, can be selected from such structures as
polyoxy(alk-di-yl), polyoxy(ar-di-yl), dioxy(alkar-di-yl), polyoxy(aralk-

di-yl), polythio(alk-di-yl), polythio(aralk-di-yl), polythio(ar-di-yl),
polythio(alkar-di-yl), polythio(aralk-di-yl), polyamido(alk-di-yl),
polyamido(ar-di-yl), polyamido-(aralk-di-yl), polycarbonyloxy(alk-di-yl),
polycarbonyloxy(ar-di-yl), polycarbonyloxy(alkar-di-yl), polycarbonyloxy-
5   (aralk-di-yl), polycarbonyldioxy(alk-di-yl), polycarbonyldioxy(ar-di-yl),
polycarbonyldioxy(alkar-di-yl), polycarbonyldioxy(aralk-di-yl),
polyamino(alk-di-yl), polyamino(ar-di-yl), polyamino(alkar-di-yl),
polyamino(aralk-di-yl), polycyclimido(ar-di-yl), polycyclimido(alkar-di-
yl), polycyclimido(aralk-di-yl), polycarbonyl(alk-di-yl), polycarbonyl(ar-
10 di-yl), polycarbonyl(alkar-di-yl), polycarbonyl(aralk-di-yl), polyimido-
(alk-di-yl), polyimido(ar-di-yl), polyimido(alkar-di-yl), polyimido(aralk-
di-yl), polyureylene(alk-di-yl), polyureylene(ar-di-yl), polyureyl-
ene(aralk-di-yl), polyureylene alkar-di-yl), polycarboxamideoxy(alk-di-
yl), polycarboxamideoxy(ar-di-yl), polycarboxamideoxy(alkar-di-yl),
15 polycarboxamideoxy(alkar-di-yl), polycarboxamideoxy(aralk-di-yl), ar-di-
yl, alkaryl-di-yl, aralkyl-di-yl and alkenoic-di-yl. Preferred divalent
linking groups, -L'-, include di(carbonyloxy)hydrocarbylene, siloxy,
dicarboxamidohydrocarbylene, di(oxycarbonyl)hydrocarbylene,
dithiohydrocarbylene, and hydrocarbylene groups containing aromatic rings.

20   During batch processing, the mercaptosulfonic acid catalyst was
suitably present in an amount sufficient to enable condensation of the
phenol with the ketone/aldehyde in a reasonable time. Preferably, the
amount of mercaptosulfonic acid ranges from 0.01 equivalents to 2.0
equivalents of catalyst per 1.00 equivalents of the ketone/aldehyde. More
25 preferably, the amount of mercaptosulfonic acid catalyst was from 0.02 to
1.0 equivalent of mercaptosulfonic acid per equivalents of
aldehyde/ketone. Most preferably, the reaction mixture will contain from
0.03 to 1.0 equivalent of mercaptosulfonic acid per equivalents of
aldehyde or ketone under batch processing.

30   When ketone/aldehyde was added over the course of a reaction (for
example, a continuous reaction) the previously stated preferred amounts
refer to total catalyst and reactants added rather than catalyst present
in a reaction mixture at a given moment. Those skilled in the art
recognize that when a reactant was added incrementally or continuously,
35 there was often a large excess of catalyst. The ratio of catalyst to
ketone/aldehyde in the reaction mixture was advantageously greater than
one, conveniently on the order of 20 equivalents to 1 equivalent.

Due to the high activity of the mercaptosulfonic acid catalysts, good reaction rates and high selectivity can be obtained at temperatures below the melting point of phenol. The phenol reactant can advantageously be kept in the liquid state by addition of solvents, for example, water,

5   methylene chloride, diphenylmethane. Low temperature reactions were often particularly advantageous, because the product diphenolic compounds crystallize in the reaction mixture and because lower reaction temperatures favor higher selectivity toward 4,4-bisphenolic products.

The reaction temperature will accordingly advantageously be selected

10   in the range from 0°C to 100°C, preferably from 15°C to 60°C. Temperature ranges can be chosen by routine experimentation, depending upon the ketone/aldehyde and phenol feeds.

When excess phenolic compound was used as solvent, the temperature for the condensation was advantageously selected so that the phenol was in

15   the liquid state. In the case of high-melting phenols, for example, those melting above 180°C, the use of an inert solvent was preferred. Diphenylmethane has been found to be particularly useful for this purpose. Other useable inert solvents include, but were not limited to, the xylenes, mesitylene, the durenes, fluorobenzene, toluene, cyclohexane,

20   chlorobenzene, halogenated aliphatic hydrocarbons and alkylnaphthalenes having low melting points.

If a solvent/diluent was used, the amount used conveniently ranges from 5 mL to 1 L per mole of ketone or aldehyde. Preferably, from 200 mL to 400 mL were used per mole of ketone or aldehyde.

25   The addition of water, generally in an amount up to a maximum of 5 percent by weight of total feed, was considered highly desirable in processes for the preparation of bisphenol A, because water lowers the freezing point of phenol and addition of water permits the condensations to be run at lower temperatures. Most preferably, the amount of added

30   water was from 1 percent by weight to 5 percent by weight of total feed.

The reaction can advantageously be carried out by stirring the ketone or aldehyde and mercaptosulfonic acid into molten phenol in such a way that the temperature in the reaction vessel will not rise above 150°C.

The molar ratio of phenolic reactant to ketone or aldehyde was

35   advantageously selected so that at least two moles of phenol will condense with the ketone to produce a corresponding bisphenol or higher condensate. Therefore, molar ratios of 2:1 or higher will advantageously be selected.

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It was preferred to carry out the reactions using larger excesses of
phenolic reactant, up to as much as 50 moles of phenol per mole of ketone
or aldehyde. It will be understood that the excess phenol acts as a
solvent or diluent, as well as a reactant.

5   Lower ratios of phenol to ketone/aldehyde were generally accompanied
by an increase in the amount of by-products formed. In the preparation of
polyphenols, it has been found that molar ratios from 2:1 to 30:1 of
phenol to aldehyde/ketone were preferred. More preferably, the reaction
mixtures will contain from 4:1 to 25:1 molar ratios of phenol to
10   aldehyde/ketone. Most preferably, the molar ratio was from 6:1 to 25:1.
          Since the condensation reaction was exothermic, the reactants,
instead of being mixed together all at once, were optionally progressively
mixed together at a speed depending upon the intensity of the cooling
employed to maintain the temperature of the reaction medium within the
15   optimum limits. After the mixing of the reactants, they were preferably
left in contact for some time in order to complete the condensation. The
duration of the introduction of the reactants during a batch process
conveniently varies from 15 minutes to 1 hour.
          In batch processes, the reactants and the catalyst were preferably
20   thoroughly stirred mechanically to assure better mixing, and hence an
improved space-time yield.
          When the process of this invention was conducted batch wise, the
reaction time was advantageously in the range of 0.1 to 20 hours depending
on the reaction conditions including the amount of the catalyst used, the
25   reaction temperature, and specific reactants, solvents and products.
          The process of this invention can also be run in a continuous mode,
more preferably by use of a series of continuous stirred tank reactors,
the use of which approximates plug flow reaction conditions. It was
preferred to carry out the process of this invention under continuous
30   reaction conditions.
          The pressure in the reaction zone was not critical, but preferably
ranges from 0.001 to 10 bar (0.1 to 1000 kPa), and more particularly from
0.5 to 3 bar (50 to 300 kPa). In many cases, it will be preferred to
carry out the reactions under ambient pressure, that was, 1 bar (100 kPa).
35   During the reaction, one mole of water was evolved for each mole of
ketone/aldehyde undergoing the condensation with phenol. It has been
found that adding water to the reaction mixtures can be advantageous for

decreasing the melting point of phenol. The water evolved during the
reactions need not be removed by distillation/entrainment with an inert
solvent in order to attain high reaction rates. In some cases, however,
it will be preferred to entrain and remove water from the reaction

5   mixture, in order to increase reaction rates.

It has been found that the soluble mercaptosulfonic acid catalysts
can advantageously be removed from the crude product by extraction with
water. The aqueous extracts can be concentrated and recovered
mercaptosulfonic acid catalyst can be optionally recycled to subsequent

10   runs. When the phenolic starting material was phenol, a solution of the
mercaptosulfonic acid in phenol was conveniently recovered and was
optionally recycled without further purification.

The acid concentration can be reduced below the limits of detection,
and probably below 1 ppm by weight of acid, by repeated extractions with

15   water. The facile removal of catalyst from the reaction mixtures was a
significant advantage over the prior art, using mixtures of condensing
agents. It was within the practice of this invention to remove the
mercaptosulfonic acid by continuous countercurrent extraction.

The time for phase separation during extraction of the acid catalyst

20   was on the order of 10 to 15 minutes under batch conditions, without a
drag layer. Stirring speed during the extraction in a mixer/settler was
adjusted so as to avoid emulsion formation.

The soluble mercaptosulfonic acid catalysts can also be removed from
reaction mixtures by extraction with a solution of an alkali metal

25   hydroxide, carbonate or bicarbonate.

In addition, the soluble mercaptosulfonic acid catalysts can be
removed from reaction mixtures by passing the reaction mixture through a
column of anion-exchange resin or amine resin, such as DOWEX™ WGR, from
The Dow Chemical Company.

30   A water purge from the process will contain phenol plus catalyst.
This purge was advantageously treated to remove phenol by extraction with
methyl isobutyl ketone before being sent to a bio-pond for disposal.

For isolation of BHPF from reaction mixtures, made using a soluble
catalyst, a phenol/water mixture was preferably distilled from the water-

35   washed mixture until the weight ratio of phenol:BHPF was below 1.5:1.
Most preferably, phenol was removed until the phenol:BHPF weight ratio was
from 1.5:1 to 0.5:1. It has been found particularly advantageous to

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dissolve the resulting material in hot methylene chloride and cool the
resulting solution to obtain crystalline BHPF.

     Very highly purified BHPF accordingly can be obtained by a process
wherein a resulting crude product was washed with water to remove $(HS)_a$-θ-

5    $(SO_3H)_b$; the resulting acid-free mixture was distilled to remove phenol and
water until the phenol:9,9-bis-(4-hydroxyphenyl)fluorene weight ratio was
less than 1.5; the resulting mixture was taken up in hot methylene
chloride and the resulting solution was cooled to produce crystalline 9,9-
bis-(4-hydroxyphenyl)fluorene. BHPF purified in this way can be used to

10   make ultrahigh quality polycarbonate resins.

     Excess phenol can also be removed by boiling the reaction mixture
repeatedly with water, optionally with the use of a water-miscible organic
solvent such as methanol. The aqueous solution was separated each time
and the product, then practically pure, was dried. Another effective

15   method of removing excess phenol was by steam distillation.

     The reaction product solution was optionally then concentrated by
evaporation and repeatedly extracted with boiling water for the removal of
excess phenol. The product so obtained was optionally then recrystallized
for further purification.

20   BHPF can be isolated from the reaction mixtures in several
additional ways. The method selected will depend on the degree of
purification desired, as well as the composition of the reaction mixture,
and the desired production rate.

     When extensive purification was undesirable or inappropriate, the

25   mixture, after being treated to remove catalyst, can be treated with a
volume of hot water sufficient to dilute the mixture and bring
precipitation of BHPF. Alternatively, the reaction mixture can be added
to hot water and the phenol removed in the form of a water/phenol
azeotrope until the phenol content was lowered sufficiently to permit

30   precipitation of BHPF from the mixture. The BHPF solids can be collected
and dried before use or can be used in the form of a slurry.

     When more extensive purification of BHPF was desired, the solids can
be purified by precipitation from a solvent, for example, diphenylmethane
or methylene chloride.

35   Another method for isolating BHPF comprises adding to the reaction
mixture, at the end of the reaction, a solvent, boiling at a higher
temperature than phenol, and removing phenol from the phenol/BHPF/solvent

mixture until BHPF crystallizes or precipitates from the mixture. This
method can be carried out by adding diphenylmethane or triisopropylbenzene
to a reaction mixture, from which catalyst has been extracted or removed,
prior to distilling the mixture. Alternatively, the solvents can be added
5   to the initial reaction mixture so that the reactions were run in the
presence of the solvent. The reaction mixture was worked up, by
extraction, to remove catalyst and then by distillation to remove solvent
and phenol, until BHPF crystallization occurs.

       BHPF can also be isolated by adding to a reaction mixture a solvent,
10   which boils at a higher temperature than phenol and dissolves sufficient
BHPF, in the absence of phenol, that removing phenol from the
phenol/BHPF/solvent mixture provides a homogeneous solution, cooling of
which causes crystallization of BHPF. Solvents meeting these requirements
include diphenylmethane, diphenyl ether, dodecane, naphthalene, Isopar™
15   (hydrocarbon mixture commercially available from Exxon Corporation) and
triisopropylbenzene.

       Further purification can also be accomplished, after removing
catalyst from the reaction mixture, by distilling to remove phenol to a
level at which BHPF crystallizes from the phenol/BHPF mixture. The BHPF
20   solids obtained can be isolated by conventional means and then further
treated, for example, by washing with water to remove phenol.

       An alternative method for obtaining high purity BHPF comprises
removing catalyst from the reaction mixture, distilling phenol from the
reaction mixture to a phenol/BHPF level such that dilution of the
25   distillation residue with a solvent induces crystallization of the BHPF
from the phenol/BHPF/solvent mixture. For example, phenol can be removed
by distillation until the distillation residue contained 50 percent by
weight of phenol and 50 percent by weight of BHPF. Methylene chloride,
triisopropylbenzene or toluene can be added to the residue and the
30   resulting solution can be cooled to bring about crystallization of highly
purified BHPF.

       Another procedure for isolating pure BHPF solid from the reaction
comprises removing the mercaptosulfonic acid catalyst, distilling phenol
from the resulting mixture, to produce a still residue, to which addition
35   of a solvent induces crystallization of BHPF. For example, a still
residue containing 80 percent by weight of phenol and 20 percent by weight

of BHPF can be diluted with a solvent, for example dichloromethane or toluene, to induce crystallization of BHPF.

In addition, BHPF can be isolated from a reaction mixture, by removing the mercaptosulfonic acid catalyst, adding to the resulting

5 reaction mixture a solvent, which forms an azeotrope with phenol and in which BHPF was soluble in the absence of phenol, and removing phenol from the mixture by azeotropic distillation. Cyclohexanol was exemplary of a solvent, which will form an azeotrope with phenol and from which BHPF will precipitate upon cooling the still residue from the azeotropic

10 distillation.

Similarly, phenol can be removed from the reaction mixtures by addition of a solvent, which forms an azeotrope with phenol. After removing phenol by azeotropic distillation, the still residue was cooled and BHPF crystallizes out from the cooled mixture.

15 In any of the purification processes which result in a crystalline product, the catalyst was optionally not removed before crystallization of product but rather either tolerated in the product or removed from the crystals, for instance by washing or other means within the skill of the art, after crystallization.

20 In some cases, the condensation of phenol with ketones or aldehydes can be run in a solvent, for example, methylene chloride, from which the product will precipitate during the course of the reaction, as was described in more detail for the preparation of bisphenol A.

A representative solvent used for crystallization of BHPF, methylene

25 chloride, can be recovered from the mother liquors by batch distillation and recycled back to the process. The still bottoms contain BHPF and methylene chloride and can be cooled to recover additional BHPF. BHPF crystals thus formed were conveniently recovered using a basket centrifuge or pressure filter and can be recycled back to a main crystallizer. Crude

30 mother liquor can also be recycled back to the phenol evaporation section.

When methylene chloride was used as solvent for crystallizing BHPF, a common vent header for collecting all vents from storage tanks and safety relief systems was recommended. The vent header system advantageously includes a flow measurement device in the inlet to a carbon

35 adsorption unit and a VOC analyzer for the exit gas. The exit gas should contain less than 100 ppm of methylene chloride. A complete effluent treating system will advantageously include means for removing organics

from process waters and means for removal of particulates from vent gas,
for example, a water venturi flow meter to scrub particulates from the
vent header.

   A further advantage of the catalysts used in the practice of this
5   invention was that the catalysts can be used to isomerize the crude
product mixture, which typically contained (4-hydroxyphenyl)(2-
hydroxyphenyl) compounds, the major bis-(4-hydroxyphenyl) compounds, and
condensates, to produce more of the bis-(4-hydroxyphenyl) compounds.

   Isomerization of a geminal bisphenol using the catalysts of the
10   invention was useful when practiced with the process of the invention or
separately, for example, after product formation using catalysts within
the skill of the art. For instance, a mixture of p,p-
bis(hydroxyphenyl)fluorene and o,p-bis(hydroxyphenyl)fluorene was
contacted with a mercaptosulfonic acid catalyst, preferably of the formula
15   $(HS)_a-\Phi-(SO_3H)_b$ or of formula (a)
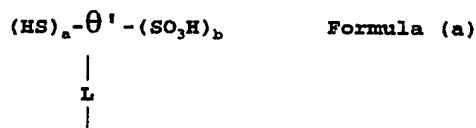
$$(HS)_a-\theta'-(SO_3H)_b \qquad \text{Formula (a)}$$
$$|$$
$$L$$
$$|$$

20

in which θ' was an alkylene, cycloaliphatic, arylene, alkylenearylene,
alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic
residue; a and b were independently selected from integers from 1 to 20; L
was an optional linking group and - was a bond, which catalytically-
25   active species was attached by the bond - to an insoluble organic or
inorganic support; and heated sufficiently to result in formation of the
p,p (bis(4-hydroxyphenyl) product from at least a portion of the o,p (2-
hydroxyphenyl, 4-hydroxyphenyl product. The catalyst was a compound
(including polymer) of the formula $(HS)_a-\Phi-(SO_3H)_b$ or of formula (a),
30   preferably those preferred for the reaction of an aldehyde or ketone with
a phenol as described herein, with 3-mercaptopropanesulfonic acid most
preferred. It was noted that such catalysts result in conveniently fast
isomerization and less formation of additional by-products than do acids
such as methane sulfonic acid. Temperatures, which will vary with the
35   compound being isomerized, were suitably any temperature at which
isomerization takes place, and were conveniently at least room temperature
(30°C), preferably at least 40°C, more preferably at least 50°C. The
temperature was preferably lower than that temperature at which an

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undesirable amount of additional by-product or polymer would form, conveniently less than 100°C, more preferably less than 85°C, most preferably less than 75°C. Seventy degrees centigrade was a convenient and preferred temperature. It was found that increasing the temperature

5   within the range speeds isomerization. Likewise, increasing the concentration of catalyst increases isomerization. Catalyst was preferably present in any amount sufficient to result in isomerization. Less was needed at higher temperatures to obtain a desirable rate of isomerization. Conveniently, the catalyst was present in the same amounts

10   and preferred ranges as for preparation of a bisphenol by the process disclosed herein. The pressure was not critical, but was also conveniently within the preferred ranges for the process of preparing bisphenols by the process herein. Time for the isomerization was preferably that in which, under the conditions, results in isomerization

15   of at least a portion, more preferably a predetermined or desired fraction of the o,p by-product being isomerized to the desired p,p product. More preferably the ratio of o,p to p,p product was less than 0.12, most preferably less than 0.1, even more preferably less than 0.075. The time to achieve this result varies with isomerization conditions but was

20   conveniently less than a day, more preferably less than 12 hours, most preferably less than 8 hours, for conversion of half of the o,p product to p,p product.

The mercaptosulfonic acid catalysts of this invention were considerably less corrosive to stainless steel than the mixed catalysts

25   used previously. Corrosion rates for stainless steel, below 0.00254 cm/year, have been measured. The reaction mixtures were believed to be substantially free of halide ions, wherein "substantially free" means less than 5000 ppm of chloride ions.

The process of this invention was advantageously carried out under

30   conditions such that the concentration of chloride was below 5000 ppm, preferably below 1000 ppm, most preferably below 100 ppm.

It was believed that the low corrosion rate was related to the absence of mineral acids, such as hydrochloric acid or sulfuric acid, from the reaction mixtures. The occurrence of corrosion in reactions using

35   mineral acids has been noted by Knebel et al., '594 and Faler '995, supra.

The insoluble catalysts of this invention can be filtered from the reaction mixtures, washed with a mixture of ketone/aldehyde and phenol,

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and recycled to subsequent runs. Alternatively, the insoluble catalysts
were used in fixed beds and the condensations of phenols with
aldehyde/ketone was done in continuous upflow, crossflow or downflow
fashion. When fixed-bed catalytic reactors were used, the catalytically-
5   active resins remain in the resin beds and need not be removed.

    Further embodiments of this invention will be determined by the
reactants used, the catalyst selected, the diluent, if any, and the
reactor employed.

    For example, when using a soluble catalyst for the condensation of
10   phenol with 9-fluorenone, without a diluent, other than excess phenol or
in the presence of a diluent which does not cause precipitation of
product, it will generally be preferred to use a high ratio of phenol to
fluorenone to maximize selectivity to the desired bisphenol product.

    A particularly preferred process was one wherein the molar ratio of
15   phenol:fluorenone was from 4:1 to 25:1; the reaction temperature was from
25°C to 50°C; the catalyst was mercaptopropanesulfonic acid or
mercaptobutanesulfonic acid, used in an amount from 5 to 10 molar percent
with respect to fluorenone; the process was carried out under ambient
pressure or under vacuum to remove water of reaction and increase the
20   reaction rate; no cosolvent was used; the catalyst was removed from the
product by extraction with water using a wash column or by batch
extraction; the water extracts thus obtained were concentrated and
recycled to the process; the product was isolated by removing excess
phenol to a weight ratio from 1.5:1 to 0.5:1 of phenol:BHPF and the
25   product was precipitated with dichloromethane.

    When an insoluble catalyst was used, a particularly preferred
process was one wherein the molar ratio of phenol:fluorenone was from 4:1
to 25:1; the condensation was carried out at a temperature from 40°C to 60°
C; no cosolvent was used; the catalyst was PMBSA; the condensation was
30   carried out in a continuous plug flow reactor; the reaction was carried
out at ambient pressure or under reduced pressure to remove water of
reaction and increase the reaction rate; the product was isolated by
removing excess phenol to a weight ratio from 1.5:1 to 0.5:1 of
phenol:BHPF and the product was precipitated with dichloromethane.

35   The process for making BHPF can also be carried out at molar ratios
of phenol:fluorenone from 7:1 to 5:1 in the presence of 0.05 to 0.15
equivalent of MPSA or MBSA per mole of fluorenone, wherein methylene

chloride was added to the reaction mixture after conversion of at least 20 percent of fluorenone has occurred; heating the resulting mixture under reduced pressure to remove an azeotrope of methylene chloride and water; and cooling the mixture at the end of the condensation reaction to cause
5   precipitation of BHPF.

The condensation of phenol with fluorenone can further be carried out using a feed containing from 5:1 to 3:1 molar ratio of phenol:fluorenone and from 0.05 to 0.15 equivalent of MPSA or MBSA per mole of fluorenone, diluted with from 10 percent by weight to 30 percent
10   by weight of methylene chloride. Crystalline BHPF can be collected from the cooled reaction mixture.

In addition, BHPF can be prepared from a reaction mixture, containing from 18:1 to 12:1 molar ratios of phenol:fluorenone and 0.025 to 0.075 equivalent of MPSA or MBSA per mole of fluorenone at a
15   temperature from 50°C to 80°C, wherein the mixture at the end of the reaction was diluted with 10 to 20 volumes of water to extract mercaptosulfonic acid catalyst, the thus-washed mixture was distilled to a phenol:BHPF weight ratio from 1.5:1 to 1:1 and cooled to bring crystallization of BHPF. The crystalline BHPF was
20   removed by filtration and washed with methylene chloride and then with water.

A process in which the product was precipitated in the reaction mixture was preferred for the preparation of bisphenol A, more particularly a process wherein the phenol:acetone feed contained from 6:1
25   to 15:1 molar ratios of phenol:acetone; the condensation was carried out at a temperature from 25°C to 35°C; the reaction mixture contained up to 5 percent by weight of water to lower the freezing point of phenol; the catalyst was 3-mercaptopropanesulfonic or 4-mercaptobutanesulfonic acid in an amount from 0.05 to 0.50 equivalent per mole of acetone in the
30   acetone:phenol feed; the reaction was carried out under ambient pressure; and the crystalline bisphenol A produced by the process was removed by filtration or centrifugation.

Further processing can include washing the bisphenol A with water to partially remove soluble catalyst, and removing additional soluble
35   catalyst by treatment with an anion exchange resin. It was believed that a preferred reactor configuration for this process was a series of

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continuous stirred tank reactors, so as to approximate plug flow reaction conditions.

Other process variations, include, but were not limited to:

(a)   preparation of bisphenol A in neat phenol, using a soluble catalyst, with precipitation of bisphenol A in the reaction mixture and

(b)   preparation of bisphenol A in phenol with a complex-forming cosolvent and soluble catalyst, with precipitation of bisphenol A in the reaction mixture.

More particularly, it was preferred to select a catalyst wherein at least 99 percent of the bisphenol A that crystallizes during the reaction was 4,4-bisphenol A. Such catalysts include soluble mercaptosulfonic acids in which a and b were each independently integers from 1 to 4. Preferred conditions include reaction temperatures from 0°C to 50°C, more preferably from 20°C to 40°C.

Representative complex-forming solvents for bisphenol A include diethyl ether, acetone, ethanol, propanol, dioxane, acetic acid, acetonitrile, methylene chloride or carbon tetrachloride. The complex-forming solvents complex preferentially with the 4,4-diphenolic isomer so that the resulting complex has solubility properties, differing from that of the uncomplexed 2,4-diphenolic compound and can be readily separated therefrom.

These processes can be run under varying pressure and temperature conditions, as well as reactant, cosolvent and catalyst concentrations, as can be determined by routine experimentation.

In one aspect, a most preferred process of this invention was that wherein the ketone was 9-fluorenone, the phenol was unsubstituted and the product was 9,9-bis-(4-hydroxyphenyl)fluorene; the molar ratio of phenol to fluorenone was from 8:1 to 25:1; the reaction mixture contained from 0.05 to 0.20 equivalent of mercaptosulfonic acid per mole of fluorene; the mercaptosulfonic acid compound was 3-mercaptopropanesulfonic acid or 4-mercaptobutanesulfonic acid and the process was carried out at a temperature from 45°C to 60°C.

An equally preferred process was that wherein the ketone was acetone, the phenol was unsubstituted and the product was 2,2-bis-(4-hydroxyphenyl)propane; the molar ratio of phenol to acetone was from 6:1 to 15:1; the reaction mixture contained from 0.10 to 0.50 equivalent of mercaptosulfonic acid per mole of acetone; the mercaptosulfonic acid

compound was 3-mercaptopropanesulfonic acid or 4-mercaptobutanesulfonic
acid and the process was carried out at a temperature from 15°C to 60°C.

Without further elaboration, it was believed that one skilled in the
art can, using the preceding description, utilize the present invention to
5   the fullest extent. The following preferred specific embodiments were,
therefore, to be construed as merely illustrative and not limitative of
the remainder of the disclosure in any way whatsoever.

In the following examples, the temperatures were set forth
uncorrected in degrees Celsius. Unless otherwise indicated, all parts and
10   percentages were by weight.

Reactor Design 1: A 500-mL reactor prepared from PFA Teflon®
(material from DuPont) was fitted with a thermocouple port, water
condenser topped with nitrogen inlet, mechanical stirrer, drain port, and
sampling port. Heating was provided with an infrared heat lamp and the
15   temperature was controlled with an electronic thermometer/temperature
controller.

Reactor Design 2: A capped 4-dram glass vial with a magnetic
stirrer. Heating was regulated by placing the vial in a temperature-
controlled aluminum block heater.

20   Reactor Design 3: A 100-mL jacketed glass reactor was fitted with a
thermometer port, magnetic stirrer, nitrogen inlet, and sampling port.
Heating was provided and the temperature was controlled by circulating
glycol solution of the appropriate temperature through the jacketed flask
using a Neslab Model RTE-220 circulating bath.

25   Reactor Design 4: A 1.5 L, 2 L, or 3 L jacketed glass reactor
fitted with a thermometer/sampling port, nitrogen inlet, and mechanical
stirrer. Heating was provided and the temperature was controlled by
circulating glycol solution of the appropriate temperature, through the
jacketed flask using a Neslab Model RTE-220 circulating bath.

30   Analytical Method 1: A Varian HPLC System (Model 9010 solvent
delivery system, Model 9095 Autosampler, Model 9065 Polychrom diode array
detector) interfaced with a Varian Star workstation was used for analysis.
Area percent analysis was reported at 282 nm. Percent conversion was
determined by an external standard method using calibrated concentration
35   curves for each major component. Analytical HPLC samples were prepared by
careful quantitative dilution of reaction samples (range: 400-500 times
dilution). Column: Waters Nova-Pak C-18 (60 Angstrom, 4 micron, 3.9 X

150 mm). Chromatography conditions: flow rate 1.0 mL/min, solvent
gradient (solvent A = water, solvent B = acetonitrile) 0 minutes: 65
percent A/35 percent B, 9 minutes: 60 percent A/40 percent B, 18 minutes:
55 percent A/45 percent B, 24 minutes: 45 percent A/ 55 percent B, 48

5   minutes: 5 percent A/ 95 percent B, 52 minutes: method end (10 minutes
equilibration before and after runs).

     Analytical Method 2: A Hewlett-Packard HPLC system (Model 1084B
solvent delivery system, Model 79850B LC terminal) was used for analysis.
Area percent analysis was reported at 254 nm. Percent conversion was

10   determined by an external standard method using calibrated concentration
curves for each major component. Analytical HPLC samples were prepared by
careful quantitative dilution of reaction samples (range: 400-500 times
dilution). Column: Waters Nova-Pak C-18 (60 Angstrom, 4 micron, 3.9 X
150 mm). Chromatography conditions: flow rate 1.0 mL/min, solvent

15   gradient (solvent A = water, solvent B = acetonitrile) 0 minutes: 65
percent A/35 percent B, 9 minutes: 60 percent A/40 percent B, 18 minutes:
55 percent, A/45 percent B, 24 minutes: 45 percent A/ 55 percent B, 36
minutes: 25 percent A/ 75 percent B, 38 minutes: 65 percent, A/35 percent
B, 38 minutes: method end. NOTE: This method gives a smaller response

20   (approximately one-half the area) for the 2,4-BHPF and the two:three
adduct BHPF peaks relative to the 4,4- BHPF peak than either methods 1 or
3 using the diode array detector.

     Analytical Method 3: A Varian HPLC system (Model 9010 solvent
delivery system, Model 9095 Autosampler, Model 9065 Polychrom diode array

25   detector) interfaced with a Varian Star workstation was used for analysis.
Area percent analysis was reported at 282 nm. Percent conversion was
determined by an internal standard method using a solution of 0.0508
weight percent acetophenone in 60/40 (weight/weight percent)
methanol/water for preparing the samples. Analytical HPLC samples were

30   prepared by careful quantitative dilution of reaction samples. Column:
Waters Nova-Pak C-18 (60 Angstrom, 4 micron, 3.9 X 150 mm).
Chromatography conditions: flow rate 1.0 mL/min, solvent gradient
(solvent A = water, solvent B = methanol) 0 minutes: 55 percent A/45
percent B, 20 minutes: 15 percent A/85 percent B, 25 minutes: 10 percent

35   A/90 percent B, 30 minutes: 55 percent A/ 45 percent B, 35 minutes:
method end (10 minutes equilibration before and after runs).

Analytical method 4:   The experimental setup of Method 1 was used. The chromatography conditions were: flow rate 1 mL/min, solvent gradient (solvent A = water, solvent B = methanol) 0 minutes: 55 percent A/45 percent B, 20 minutes: 15 percent A/85 percent B, 25 minutes 10 percent A/90 percent B.   Analysis - Internal Standard method using 0.0508 percent acetophenone in 60 percent methanol/water.   Average relative standard deviations ranges from 1 to 2 percent, depending upon peak analyzed.

Analytical Method 5:   The reaction mixture was diluted with acetonitrile to a concentration of 0.01-0.1 percent by weight of components and the diluted sample was analyzed by HPLC on a Waters NovaPak C18 column (10.16 cm x 0.635 cm inner diameter) connected to a Varian™ 9100 UV detector, set at 280 nm. The column temperature was 30°C, the pressure was 140 (14,000 kPa) at 0 minutes, the absorption full scale for the detector was 2.0, the integrator attenuation was 3 and the chart speed was 0.5 cm/minutes.   The auto sampler injects 20 microliters of sample onto the column every 36 minutes.   Reservoir A contained megapure water and reservoir B HPLC grade acetonitrile. The following protocol was used:

Time	Flow Rate	%B
(min)	(mL/min)	
0	1.0	40
8	1.0	40
20	1.0	60
26	1.0	99
30	1.0	40

The peak area generated by each component in the sample was used with its known response factor, and the dilution ratio, to calculate the concentrations of each component in the sample solution.

Fluorenone (Aldrich 98 percent), about 0.5 percent fluorene and methyl-fluorenes

Acetone (Baker reagent, dried over molecular sieves)

Diphenylmethane (Penta International, 99+ percent distilled grade)

Phenol (Dow Chemical 99+ percent), about 100 ppm H_2O + 100 ppm impurities

Sodium 3-mercaptopropanesulfonate: Source A: 90 percent purity (Aldrich)

Source B: 90 percent purity (Raschig Corp.)

3-Mercaptopropanesulfonic acid (MPSA):

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Source A: Prepared from 90 percent Aldrich sodium

3-mercaptopropanesulfonate by reaction with HCl or treatment in an

ion-exchange column

Source B: Prepared from 90 percent Raschig Corp. sodium 3-

5   mercaptopropanesulfonate

Sodium 2-mercaptoethanesulfonate: 98 percent (Aldrich)

4-Mercaptobutanesulfonic acid (MBSA): prepared from

1,4-butanesultone (Aldrich) by reaction with NaSH, Ba(SH)$_2$ or an alkali

metal thioacetate in accordance with R. Fischer, supra, A. Mustafa, supra,

10   or Chem. Abs., 90:86742m (1979).

2-Benzyl-4-mercaptobutanesulfonic acid: prepared from

1,4-butanesultone (Aldrich) and benzyl bromide in accordance with M. B.

Smith et al., "Lithium Aluminum Hydride-Aluminum Hydride Reduction of

Sultones," J. Org. Chem., Volume 46 (1981), Pages 101-106 or T. Durst et

15   al., "Metallation of 5- and 6-membered ring sultones," Can. J. Chem.,

Volume 47 (1969), Pages 1230-1233.

2,3-Dimercaptopropanesulfonic acid: prepared from sodium

2,3-dimercaptopropanesulfonate (Aldrich, 95 percent) by neutralization

with HCl or treatment with an acid ion-exchange resin, for example, DOWEX™

20   MSC-1, from The Dow Chemical Company.

2,2-Bis(mercaptomethyl)-1,3-propanedisulfonic acid: prepared from

2,2-bis(bromomethyl)-1,3-propanediol (Aldrich, 98 percent) as follows:

A mixture of 2,2-bis-(bromomethyl)-1,3-propanedisulfonic acid (200.0

g, 0.764 mol, 1.00 equivalent) and sodium sulfite (211.7 g, 1.68 mol, 2.20

25   equivalents) in 500 mL of deionized water was allowed to react under

reflux (108°C) for 28 hours. At this time, additional sodium sulfite

(105.9 g, 0.840 mol, 1.10 equivalent) was added and the mixture was

allowed to react for 3 additional days under reflux. At this point, the

mixture consists of a clear solution and a considerable amount of solids.

30   The mixture was cooled to room temperature and saturated with

gaseous hydrogen chloride. An exotherm to 43°C was observed. The mixture

becomes homogenous and yellow in color during the early stages of HCl

addition. As the mixture becomes saturated with HCl, a voluminous white

precipitate was formed. The solution was cooled to room temperature and

35   filtered to remove solid salts, which were primarily sodium chloride and

sodium bromide. Water was removed from the filtrate to provide 2,2-bis-

(hydroxymethyl)-1,3-propanedisulfonic acid (190.7 g) as a highly viscous amber oil (glass).

Alternatively, the reaction mixture can be worked up by dilution with 200 mL of ethanol or methanol, after which the solid was removed by 5 filtration. Solvent was removed from the filtrate on a rotary evaporator, to produce a white solid containing mainly disodium 2,2-bis-(hydroxymethyl)-1,3-propanedisulfonate. Concentrated hydrochloric acid can be added to the solid product to give the soluble disulfonic acid, plus insoluble sodium chloride and sodium bromide.

10   p-Xylene (400 mL) was added to the 2,2-bis-(hydroxymethyl)-1,3-propanedisulfonic acid and the resulting two-phase mixture was heated under reflux (135°C to 150°C pot temperature) to remove water, produced by the dehydration, in the form of an azeotrope in a Dean-Stark trap. After 8 hours' heating under reflux, the mixture was allowed to cool to room 15 temperature and the upper xylene phase was decanted from the lower viscous product phase. Water (300 mL) was added to the cooled, lower phase containing 2,2-bis-(hydroxymethyl)-1,3-propanedisulfonic acid bis-sultone to produce a large mass of white solid. The white solid (bis-sultone) was removed by filtration, slurry washed extensively with water and with 20 methanol and dried in a vacuum oven

To a solution of sodium bicarbonate (9.6 g, 114 mmol, 2.6 equivalents) in 30 mL of water was slowly added thiolacetic acid (7.5 g, 96 mmol, 2.2 equivalents). The resulting solution of sodium thiolacetate was added to a solution of 2,2-bis-(hydroxymethyl)-1,3-propanedisulfonic 25 acid bis-sultone (10 g, 43.8 mmol, 1.00 equivalent) in 280 g of acetonitrile. After all the thiolacetate was added, the resulting mixture was allowed to stand overnight at ambient temperature. Solvent was removed using a rotary evaporator to give 19.6 g of ring-opened bis-(thioacetate) adduct as a tan, flaky solid.

30   The thioacetate adduct (18.2 g) was hydrolyzed by stirring overnight at ambient temperature in a nitrogen-saturated mixture of 10 percent sodium hydroxide (20 g) and 100 g of water. The mixture was acidified to pH 3 with 10 percent aqueous hydrochloric acid solution. Solvent was removed from the resulting mixture in a fume hood, using a rotary 35 evaporator. The residue was dissolved in 50 mL of water and saturated with hydrogen chloride gas. The resulting solid salt was removed by filtration and the filtrate was concentrated using a rotary evaporator to

give 2,2-bis-(mercaptomethyl)-1,3-propane-disulfonic acid as a viscous
dark-colored oil.

Alternatively, the thioacetate adduct can be hydrolyzed by stirring
with concentrated hydrochloric acid, removing the solid salt product by
5   filtration and removing water from the filtrate using a rotary evaporator.

ABBREVIATIONS

       nm = nanometers

       uv = ultraviolet

       rpm = revolutions per minute

10   mmol = millimoles

       HPLC = high pressure liquid chromatography

       BHPF = 9,9-bis-(4-hydroxyphenyl)fluorene = 4,4-isomer = BF

       MPSA = 3-mercaptopropanesulfonic acid

       MBSA = 4-mercaptobutanesulfonic acid

15   FN = Fn = 9-fluorenone

       2,4-isomer = 9-(2-hydroxyphenyl)-9-(4-hydroxyphenyl)fluorene

       DPM = diphenylmethane

       BPA = 2,2-bis-(4-hydroxyphenyl)propane = bisphenol A

       n/d = not determined

20   ~ = about or approximate

EXAMPLE 1
CONDENSATION OF 9-FLUORENONE WITH PHENOL: (3-MERCAPTOPROPANESULFONIC ACID)

       9-Fluorenone (20.0 g, 0.111 mol, 1.0 equivalent) and molten phenol
(156.7 g, 1.66 mol, 15.0 equivalents) were added to a 500 mL PFA Teflon™,
25   material from DuPont, reactor (reactor design 1).

       The reaction mixture was heated to 65°C with stirring at 300 to350
rpm under a pad of nitrogen. 3-Mercaptopropane-sulfonic acid (0.864 g,
5.53 mmol, 0.0498 equivalents) was added slowly over approximately 1
minute to the reaction mixture at 65°C. The mixture turns dark
30   yellow-orange upon adding the catalyst and gradually fades to a lighter
yellow color as the reaction progresses. A slight exotherm to 66°C was
observed. The exotherm persists for 10 minutes before the mixture cools to
the reaction temperature of 65°C. The reaction was monitored throughout
the reaction period by collecting samples and analyzing by HPLC
35   (Analytical method 1).

       The 9-fluorenone was found to be completely consumed within 120
minutes with a product composition, determined by quantitative HPLC, of 98

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percent of 9,9-bis-(4-hydroxyphenyl)-fluorene. The product was further
analyzed by a combination of HPLC and UV (282 nm) and contained:

% by area	product
96.9	9,9-bis-(4-hydroxyphenyl)fluorene (BHPF)
2.4	9-(2-hydroxyphenyl)-9-(4-hydroxyphenyl)- fluorene (2,4-isomer)
0.7	adduct containing two fluorene units and three phenolic units (two:three adduct)

EXAMPLE 2

GENERATION OF 3-MERCAPTOALKANESULFONIC ACIDS FROM THEIR SODIUM SALTS IN
THE REACTION MIXTURE

    A.   The procedure of Example 1 was repeated except that the
catalyst was prepared in situ from 90 percent sodium
3-mercaptopropanesulfonate (0.854 g, 4.79 mmol, 0.0431 equivalents) and 95
to 98 percent sulfuric acid (0.48 g, 4.9 mmol, 0.044 equivalents) and the
reaction was conducted at 85°C.

    The 9-fluorenone was completely consumed between 60 and 120 minutes,
giving a final isomer distribution, determined as in Example 1, of:

% by area	product
95.3	4,4-isomer (BHPF)
3.6	2,4-isomer
1.1	two-three adduct

    B.   The procedure of Example 2A was repeated except that 98
percent sodium 2-mercaptoethanesulfonate (0.779 g, 4.75 mmol, 0.0427
equivalents) and 95 to 98 percent sulfuric acid (0.48 g, 4.9 mmol, 0.044
equivalents) were used as catalysts. The reaction was conducted at 85°C.

    The 9-fluorenone was completely consumed within 60 minutes, giving a
product isomer distribution, as described in Example 2A, of:

% by area	product
91.7	4,4-isomer
6.6	2,4-isomer
1.7	two:three adduct

    These experiments demonstrate that 2-mercaptoethane-sulfonic acid,
generated in the reaction mixture, was an effective condensing agent for
the process.

EXAMPLE 3

CONDENSATION USING SULFURIC ACID AND 3-MERCAPTOPROPIONIC ACID (COMPARATIVE
EXAMPLE)

     9-Fluorenone (20.0 g, 0.111 mol, 1.0 equivalent) and molten phenol

5   (156.7 g, 1.66 mol, 15.0 equivalent) were added to the reactor (reactor
design 1). The reaction mixture was heated to 65°C with stirring a pad of
nitrogen. 3-Mercaptopropionic acid (0.588 g, 5.54 mmol, 0.0499
equivalent) was added to the reaction mixture at 65°C, followed by the slow
addition (over 1 minute) of concentrated (95-98 percent) sulfuric acid

10 (0.551 g, 5.62 mmol, 0.0506 equivalent) to the reaction mixture at 65°C.
The mixture turns purplish-orange upon adding the sulfuric acid and
gradually fades to a yellow-orange color within 5 to 10 minutes. A slight
exotherm to 66 to 67°C, was observed.

     The exotherm persists for 15 minutes before the reaction mixture

15 cools to the reaction temperature of 65°C. The reaction was monitored
throughout the reaction period by collecting samples and analyzing by
HPLC. The 9-fluorenone was found to be completely consumed between 240
and 420 minutes. HPLC analysis (analytical method 3) gives product
distribution:

20

% by area	product
93.0	9,9-bis-(4-hydroxyphenyl)fluorene
5.5	2,4-isomer
1.5	two:three adduct

     This example shows that the prior art process was slower than the

25 process of Examples 1 or 2 and that the resulting product contained less
of the 4,4-isomer, than produced by the process of Examples 1 or 2.

EXAMPLE 4

EFFECT OF ADDED WATER IN FLUORENONE PHENOLATIONS USING MPSA (PHENOL AS
SOLVENT)

30   A.   9-Fluorenone (138.1 g, 0.770 mol, 1.00 equivalent) and molten
phenol (1500 g, 15.9 mol, 20.8 equivalent) was added to the reactor
(reactor design 4, 2 L). The reaction mixture was heated to 45°C with
stirring under a pad of nitrogen. 3-Mercaptopropanesulfonic acid (8.28 g,
53.0 mmol, 0.0692 equivalent) was added slowly over approximately 1 minute

35 to the reaction mixture at 45°C. The reaction was monitored throughout the
reaction period by collecting samples and analyzing by HPLC. The
9-fluorenone was found to be 22 percent consumed within 9 minutes, 52

percent consumed within 30 minutes, 76 percent consumed within 1 hour, 92 percent consumed within 1.75 hours, and 100 percent consumed within 3.5 hours. HPLC analysis (analytical method 3) gives the following relative area percent analysis for the reaction products at 100 percent

5   conversion:

% by area	product
96.9	9,9-bis(4-hydroxyphenyl)fluorene
2.4	2,4-isomer
0.6	two:three adduct

10   B.   9-Fluorenone (6.44 g, 0.0358 mol, 1.00 equivalent), molten phenol (70.0 g, 0.744 mol, 20.8 equivalent), and deionized water (1.93 g, 0.107 mol, 3.00 equivalent) was added to the reactor (reactor design 3). The reaction mixture was heated to 45°C with stirring under a pad of nitrogen. 3-Mercaptopropanesulfonic acid (0.385 g, 2.47 mmol, 0.0690

15   equivalent) was added slowly over approximately 1 minute to the reaction mixture at 45°C. The reaction was monitored throughout the reaction period by collecting samples and analyzing by HPLC. The 9-fluorenone was found to be 4 percent consumed within 9 minutes, 13 percent consumed within 1 hour, 29 percent consumed within 3.5 hours, and 94 percent consumed within

20   20.5 hours. HPLC analysis (analytical method 3) gives the following relative area percent analysis for the reaction products (fluorenone area not included) at 94 percent conversion:

% by area	product
96.5	BHPF (4,4-isomer)
2.9	2,4-isomer
0.6	two:three adduct

25

       These experiments show that higher reaction rates and lower amounts of undesirable by-products were obtained, in the absence of additional water.

30   EXAMPLE 5

CONDENSATION OF FLUORENONE WITH PHENOL USING OTHER CONDENSING AGENTS

       A.   4-MERCAPTOBUTANESULFONIC ACID

       9-Fluorenone (82.9 g, 0.460 mol, 1.00 equivalent) and molten phenol (900 g, 9.56 mol, 20.8 equivalent) was added to the reactor (reactor

35   design 4, 2 L). The reaction mixture was heated to 45°C with stirring under a pad of nitrogen. 4-Mercaptobutanesulfonic acid (5.41 g, 31.8 mmol, 0.0692 equivalent) was added slowly over approximately 1 minute to

the reaction mixture at 45°C. The reaction was monitored throughout the
reaction period by collecting samples and analyzing by HPLC. The
9-fluorenone was found to be 17 percent consumed within 5.5 minutes, 58
percent consumed within 30 minutes, 83 percent consumed within 1 hour, 95
5   percent consumed within 1.75 hours, and 100 percent consumed within 3.5
hours. HPLC analysis (analytical method 3) gives the following relative
area percent analysis for the reaction products at 100 percent
conversion:

% by area	product
97.0	BHPF
2.5	2,4-isomer
0.5	two:three adduct

    B.   2,2-BIS-(MERCAPTOMETHYL)-1,3-PROPANEDISULFONIC ACID
        To a 4-dram vial (reactor design 2) was added a mixture of
15   fluorenone (0.40 g, 2.22 mmol, 1.00 equivalent) and phenol (2.10 g, 22.3
mmol, 10.0 equivalent). The capped vial was placed into the heating
control block regulated at 63°C and stirring began.
2,2-Bis(mercaptomethyl)-1,3-propanedisulfonic acid (0.029 g, 0.098 mmol,
0.044 equivalent) was added in one portion to the vial which was then
20   tightly capped. The reaction was monitored throughout the reaction period
by collecting samples and analyzing by HPLC. The 9-fluorenone was found
to be 25 percent consumed in 1.5 hours. HPLC analysis (analytical method
2) gives the following relative area percent analysis for the reaction
products (fluorenone area not included) at 25 percent conversion:

% by area	product
95.7	BHPF
3.4	2,4-isomer
0.9	two:three adduct

    C.   2,3-DIMERCAPTOPROPANESULFONIC ACID
30   To a 4-dram vial (reactor design 2) was added a mixture of
fluorenone (0.40 g, 2.22 mmol, 1.00 equivalent) and phenol (2.10 g, 22.3
mmol, 10.0 equivalent) The capped vial was placed into the heating
control block regulated at 63°C and stirring was begun.
2,3-Dimercaptopropanesulfonic acid (0.021 g, 0.011 mmol, 0.050 equivalent)
35   was added in one portion to the vial which was then tightly capped. The
reaction was monitored throughout the reaction period by collecting

samples and analyzing by HPLC (analytical method 2). The 9-fluorenone was
found to be 5 percent consumed in 1.5 hours.

     D.   3-MERCAPTOPROPIONIC ACID AND METHANESULFONIC ACID
(COMPARATIVE EXAMPLE)

5   To a 4-dram vial (reactor design 2) was added a mixture of
fluorenone (0.460 g, 2.55 mmol, 1.00 equivalent) and phenol (5.00 g, 53.1
mmol, 20.8 equivalent) The capped vial was placed into the heating
control block regulated at 55°C and stirring was begun.
3-Mercaptopropionic acid (0.0217 g, 0.204 mmol, 0.080 equivalent) and

10   methanesulfonic acid (0.0197 g, 0.205 mmol, 0.080 equivalent) were added
in one portion to the vial which was then tightly capped. The reaction
was monitored throughout the reaction period by collecting samples and
analyzing by HPLC. The 9-fluorenone was found to be 32 percent consumed
within 30 minutes, 51 percent consumed within 1 hour, and 71 percent

15   consumed within 2 hours. HPLC analysis (analytical method 3) gives the
following relative area percent analysis for the reaction products
(fluorenone area not included) at 71 percent conversion:

% by area	product
93.7	BHPF
5.5	2,4-isomer
0.8	two:three adduct

     E.   3-MERCAPTOPROPIONIC ACID AND METHYLSULFAMIC ACID (COMPARATIVE
EXAMPLE)

25   To a 4-dram vial (reactor design 2) was added a mixture of
fluorenone (0.460 g, 2.55 mmol, 1.00 equivalent) and phenol (5.00 g, 53.1
mmol, 20.8 equivalent). The capped vial was placed into the heating
control block regulated at 55°C and stirring was begun.
3-Mercaptopropionic acid (0.0217 g, 0.204 mmol, 0.080 equivalent) and

30   methylsulfamic acid (Aldrich 98 percent) (0.0227 g, 0.204 mmol, 0.080
equivalent) were added in one portion to the vial which was then tightly
capped. The reaction was monitored throughout the reaction period by
collecting samples and analyzing by HPLC. The 9-fluorenone was found to
be 13 percent consumed within 1 hour, and 21 percent consumed within 2

35   hours. HPLC analysis (analytical method 3) gives the following relative
area percent analysis for the reaction products (fluorenone area not
included) at 21 percent conversion:

% by area	product
95.4	BHPF
4.6	2,4-isomer
n/d	two:three adduct

5   F.   SUBSTITUTION OF PHOSPHONIC ACIDS FOR METHANESULFONIC ACID

(COMPARATIVE EXAMPLES)

The reaction conditions described in Example 5D were repeated

substituting each of the following acids (each at 8 mol percent) for

methanesulfonic acid in the reaction: sulfamic acid (Aldrich 98 percent),

10   methylphosphonic acid (Aldrich 98 percent), and phenylphosphonic acid

(Aldrich 98 percent). In each case, very little conversion of the

fluorenone was observed in comparison with the use of methanesulfonic

acid.

These examples demonstrate that mixtures of a mercapto-compound and

15   an acid were inferior to 3-mercaptopropane-sulfonic or 4-

mercaptobutanesulfonic acid for catalyzing the condensation of phenol with

fluorenone.

EXAMPLE 6

EFFECT OF WATER CONCENTRATION IN FLUORENONE PHENOLATIONS USING MPSA WITH

20   DIPHENYLMETHANE AS A CO-SOLVENT

A.   9-Fluorenone (3.65 g, 0.0200 mol, 1.00 equivalent), molten

phenol (39.6 g, 0.420 mol, 20.8 equivalent), deionized water (0.055 g,

3.06 mmol, 0.151 equivalent) and diphenylmethane (32.83 g) was added to

the reactor (reactor design 2). The reaction mixture was heated to 53°C

25   with stirring under a pad of nitrogen. 3-Mercaptopropanesulfonic acid

(0.170 g, 1.10 mmol, 0.0537 equivalent) was added slowly over

approximately 1 minute to the reaction mixture at 53°C. The reaction was

monitored throughout the reaction period by collecting samples and

analyzing by HPLC. The 9-fluorenone was found to be 49 percent consumed

30   within 2 hours and 77 percent consumed within 4.5 hours. HPLC analysis

(analytical method 3) gives the following relative area percent analysis

for the reaction products (fluorenone area not included) at 77 percent

conversion:

% by area	product
96.1	BHPF
3.4	2,4-isomer
0.5	two:three adduct

B.   9-Fluorenone (3.65 g, 0.020 mol, 1.0 equivalent), molten

phenol (39.6 g, 0.420 mol, 20.8 equivalent), deionized water (0.362 g,

20.1 mmol, 0.994 equivalent) and diphenylmethane (32.83 g) was added to

the reactor (reactor design 2). The reaction mixture was heated to 53°C

5   with stirring under a pad of nitrogen. 3-Mercaptopropanesulfonic acid

(0.158 g, 1.00 mmol, 0.0500 equivalent) was added slowly over

approximately 1 minute to the reaction mixture at 53°C. The reaction was

monitored throughout the reaction period by collecting samples and

analyzing by HPLC. The 9-fluorenone was found to be 25 percent consumed

10   within 2 hours, 45 percent consumed within 4.5 hours, and 57 percent

consumed within 6 hours. HPLC analysis (analytical method 3) gives the

following relative area percent analysis for the reaction products

(fluorenone area not included) at 57 percent conversion:

% by area	product
96.3	BHPF
3.7	2,4-isomer
n/d	two:three adduct

C.   9-Fluorenone (3.65 g, 0.0200 mol, 1.00 equivalent), molten

phenol (39.6 g, 0.420 mol, 20.8 equivalent), deionized water (1.09 g, 60.7

20   mmol, 3.00 equivalent) and diphenylmethane (32.83 g) was added to the

reactor (reactor design 2). The reaction mixture was heated to 53°C with

stirring under a pad of nitrogen. 3-Mercaptopropanesulfonic acid (0.158

g, 1.00 mmol, 0.0500 equivalent) was added slowly over approximately 1

minute to the reaction mixture at 53°C. The reaction was monitored

25   throughout the reaction period by collecting samples and analyzing by

HPLC. The 9-fluorenone was found to be 11 percent consumed within 2

hours, 20 percent consumed within 4.5 hours, and 23 percent consumed

within 6 hours. HPLC analysis (analytical method 3) gives the following

relative area percent analysis for the reaction products (fluorenone area

30   not included) at 23 percent conversion:

% by area	product
95.9	BHPF
4.1	2,4-isomer
n/d	two:three adduct

35   These examples show that addition of large amounts of water to the

reaction mixtures retards the condensation reaction.

EXAMPLE 7

REMOVAL OF WATER UNDER VACUUM WITH AND WITHOUT DIPHENYLMETHANE AS A

CO-SOLVENT

5   A.   9-Fluorenone (127.7 g, 0.709 mol, 1.00 equivalent) and molten

phenol (996.1 g, 10.58 mol, 14.9 equivalent) was added to the reactor

(reactor design 4, 3 L). The reaction mixture was heated to 45°C with

stirring under a pad of nitrogen. 3-Mercaptopropanesulfonic acid (5.53 g,

35.4 mmol, 0.0500 equivalent) was added slowly over approximately 1 minute

to the reaction mixture at 45 °C. The reaction was monitored throughout

10   the reaction period by collecting samples and analyzing by HPLC. The

9-fluorenone was found to be 60 percent consumed within 1 hour, 88 percent

consumed within 2 hours, and 95 percent consumed within 2.5 hours. HPLC

analysis (analytical method 2) gives the following relative area percent

analysis for the reaction products at 100 percent conversion:

15   % by area   product

98.0   BHPF

1.4   2,4-isomer

0.7   two:three adduct

B.   9-Fluorenone (127.7 g, 0.709 mol, 1.00 equivalent) and molten

20   phenol (996.4 g, 10.59 mol, 14.9 equivalent) was added to the reactor

(using reactor design four (4), three (3) L reactor with a Dean-Stark

water separation trap and vacuum inlet attached in lieu of the nitrogen

inlet). The reaction mixture was heated to 45°C with stirring.

3-Mercaptopropanesulfonic acid (5.53 g, 35.4 mmol, 0.0500 equivalent) was

25   added slowly over approximately 1 minute to the reaction mixture at 45°C.

The reaction mixture was allowed to stir for 15 minutes at atmospheric

pressure, then vacuum was applied to the reactor. From this point on, the

reaction was conducted under reduced pressure conditions (<5 mm Hg) with

water/phenol distillate collected in the Dean-Stark trap. The reaction

30   was monitored throughout the reaction period by collecting samples and

analyzing by HPLC. The 9-fluorenone was found to be 68 percent consumed

within 1 hour, 98 percent consumed within 2 hours, and 100 percent

consumed within 2.5 hours. HPLC analysis (analytical method 2) gives the

following relative area percent analysis for the reaction products at 100

35   percent conversion:

% by area	product
98.1	BHPF
1.3	2,4-isomer
0.6	two:three adduct

C.   9-Fluorenone (191.5 g, 1.063 mol, 1.00 equivalent), molten phenol (1500 g, 15.9 mol, 15.0 equivalent) and diphenylmethane (156.7 g) were added to the reactor (reactor design 4, 3 L with a Dean-Stark water separation trap and vacuum inlet attached in lieu of the nitrogen inlet). The reaction mixture was heated to 45°C with stirring. 3-Mercaptopropanesulfonic acid (8.27 g, 53.0 mmol, 0.0499 equivalent) was added slowly over approximately 1 minute to the reaction mixture at 45°C. The reaction mixture was allowed to stir for 15 minutes at atmospheric pressure, then vacuum was applied to the reactor. From this point on, the reaction was conducted under reduced pressure conditions (<5 mm Hg) with water/phenol distillate collected in the Dean-Stark trap. The reaction was monitored throughout the reaction period by collecting samples and analyzing by HPLC. The 9-fluorenone was found to be 20 percent consumed within 15 minutes, 80 percent consumed within 2 hours, 98 percent consumed within 3.5 hours, and 100 percent consumed within 6 hours. HPLC analysis (analytical method 2) gives the following relative area percent analysis for the reaction products at 100 percent conversion:

% by area	product
98.3	BHPF
1.2	2,4-isomer
0.5	two:three adduct

These results show that removal of water from the reaction mixtures, containing diphenylmethane solvent, was unnecessary. These results show that removing water from the reaction mixtures accelerated the rate of the phenolation reaction, but was not necessary for good reaction rates and conversions.

EXAMPLE 8

REACTION OF PHENOL WITH ACETONE TO PRODUCE BISPHENOL A USING MPSA CATALYST

A.   To a 4-dram vial (reactor design 2) was added a mixture of acetone (0.11 g, 1.8 mmol, 1.0 equivalent) and phenol (2.40 g, 25.5 mmol, 14.0 equivalent). The capped vial was placed into the heating control block regulated at 62°C and stirring was begun. 3-Mercaptopropanesulfonic

acid (0.021 g, 0.13 mmol, 0.070 equivalent) was added in one portion to the vial which was then tightly capped. The reaction was monitored throughout the reaction period by collecting samples and analyzing by HPLC. The acetone was found to be approximately 70 percent consumed

5   within 2 hours. HPLC analysis (analytical method 2) gives a relative area percent ratio of 97.0:3.0 for the desired reaction product 2,2-bis-(4-hydroxyphenyl)propane (4,4-bisphenol A) relative to the isomeric impurity 2-(2-hydroxyphenyl)-2-(4-hydroxyphenyl)-propane (2,4-bisphenol A) at 70 percent conversion.

10   B.   To a 4-dram vial (reactor design 2) was added a mixture of acetone (0.11 g, 1.8 mmol, 1.0 equivalent) and phenol (2.40 g, 25.5 mmol, 14.0 equivalent). The capped vial was placed into the heating control block regulated at 25°C and stirring was begun. 3-Mercaptopropanesulfonic acid (0.074 g, 0.47 mmol, 0.25 equivalent) was added in one portion to the

15   vial which was then tightly capped. The reaction was monitored throughout the reaction period by collecting samples and analyzing by HPLC. The acetone was found to be approximately 70 percent consumed within 2 hours. During the later stages of reaction, the reaction product begins to crystallize from the reaction mixture. HPLC analysis (analytical method

20   2) gives a relative area percent ratio of 98.9:1.1 for the desired reaction product 2,2-bis-(4-hydroxy-phenyl)propane (4,4-bisphenol A) relative to the isomeric impurity 2-(2-hydroxyphenyl)-2-(4-hydroxyphenyl)propane (2,4-bisphenol A) for the bulk reaction solution.

25   Separation of the crystalline product from the reaction mixture followed by rinsing of the crystals with water to remove surface impurities provides 4,4-bisphenol A product containing less than 500 parts per million of the 2,4-bisphenol A impurity.

             C.   (Comparative Example) To a 4-dram vial (reactor design 2) was

30   added a mixture of acetone (0.11 g, 1.8 mmol, 1.0 equivalent) and phenol (2.40 g, 2 5.5 mmol, 14.0 equivalent). The capped vial was placed into the heating control block regulated at 62°C and stirring was begun. 3-Mercaptopropionic acid (0.014 g, 0.13 mmol, 0.070 equivalent) and methanesulfonic acid (0.013 g, 0.13 mmol, 0.070 equivalent) were added in

35   one portion to the vial which was then tightly capped. The reaction was monitored throughout the reaction period by collecting samples and analyzing by HPLC. The acetone was found to be approximately 70 percent

consumed within 2 hours. HPLC analysis (analytical method 2) gives a

relative area percent ratio of 96.2:3.8 for the desired reaction product

2,2-bis-(4-hydroxyphenyl)propane (4,4-bisphenol A) relative to the

isomeric impurity 2-(2-hydroxyphenyl)-2-(4-hydroxy-phenyl)propane

5   (2,4-bisphenol A) at 70 percent conversion.

These experiments show that MPSA gives a product, with a higher 4,4-

isomer ratio than prior art catalysts.

EXAMPLE 9

PREPARATION OF THE POLYMER-SUPPORTED MERCAPTOSULFONIC ACID CATALYST

10   (PMBSA)

A.   PREPARATION OF SULTONE INTERMEDIATE

1,4-Butanesultone (3.00 g, 22.0 mmol, 1.00 equivalent) was added to

dry THF (150 mL) under a nitrogen atmosphere. The solution was cooled to

-78°C using a dry ice/acetone bath. n-Butyllithium (1.6 molar in hexanes,

15   13.8 mL, 1.00 equivalent) was added slowly dropwise to the -78°C solution

via an addition funnel over approximately 40 minutes with vigorous

stirring. The homogeneous reaction mixture was allowed to stir for an

additional 10 to 15 minutes at -78°C. Poly(vinylbenzylchloride) (3.3 g,

approximately 1.0 equivalent of chloromethyl groups, 60/40 mixture of 3-

20   and 4-isomers, Aldrich Chemical Co.) in dry THF (10 mL) was added over

approximately 2 minutes to the reaction mixture at -78°C. The reaction

mixture was allowed to slowly warm to room temperature in the cooling bath

over approximately 3 hours. A white precipitate forms in the reaction

mixture during the reaction period and remains as a solid as the mixture

25   reaches room temperature. Water (100 mL) was added to the reaction

mixture and the white (insoluble) solid was removed by filtration under

vacuum. The solid was slurry-washed with water, then with small volumes

of methanol and methylene chloride and dried in a vacuum oven, providing

4.77 g of a white solid sultone-functional polymer.

30   B.   CONVERSION OF THE SULTONE-FUNCTIONAL POLYMER TO POLYMER-

SUPPORTED MERCAPTOSULFONIC ACID (PMBSA)

The sultone-functional polymer from above (4.00 g, approximately

15.9 mmol sultone) was added to THF (125 mL). Potassium thioacetate (2.20

g, 19.0 mmol, 1.20 equivalent) was added as a solid to the slurry of the

35   polysultone in THF. One drop of 50 percent tetrabutylammonium chloride

was added to the rapidly stirred slurry. The temperature rose to 26°C over

several minutes, then slowly dropped to 20°C. Two additional drops of 50

percent tetrabutylammonium chloride were added and the solution was warmed
to 40°C for 15 minutes. Water (100 mL) was slowly added over 1 hour to the
reaction mixture at 40°C. Substantial solid remains in the mixture at all
stages of the reaction. The water/THF reaction mixture was allowed to
react 15 hours at 40°C. The solvent was removed by rotary evaporation and
the resultant solid was ground to a fine powder. THF (125 mL) was again
added to the solid, forming a slurry. Additional potassium thioacetate
(2.20 g, 19.0 mmol, 1.20 equivalent) was added, resulting in an exotherm
to 26°C.   Several drops of 50 percent tetrabutylammonium chloride were
added and the reaction mixture was heated to 40°C for 15 hours. The
solvent was removed by rotary evaporation. The tan solid was slurried in
a 2:1 (by volume) mixture of toluene/ethanol. Concentrated hydrochloric
acid (50 mL) was added and the mixture was stirred at room temperature
overnight. Most of the HCl was removed by sparging the mixture with
nitrogen, then the solvents were removed by rotoevaporation. The light
tan solid was slurry-washed extensively with 10 percent hydrochloric acid
and with water. Drying overnight in a vacuum oven (60°C/full vacuum)
provides 4.18 g of the polymer-supported mercaptosulfonic acid as a light
tan solid.

   C.   PREPARATION OF A GEL PMBSA CATALYST (PMBSA-MER)

        A catalyst was prepared as above, starting with Merrifield® resin
(200 to 400, 2 percent crosslinked, gel), treated with butanesultone. The
product was identified as PMBSA-MER.

   D.   PREPARATION OF CATALYST FROM BROMOMETHYLATED MACROPOROUS
POLYSTYRENE (PMBSA-XEBR)

        A catalyst was prepared as above, starting with bromomethylated
Amberlite™ XE-305 macroporous resin (4 percent crosslinked, 20 to 50 mesh,
3.7 meq Br/g).

   E.   PREPARATION OF CATALYST FROM CHLOROMETHYLATED MACROPOROUS
POLYSTYRENE (PMBSA-XECL)

        A catalyst was prepared as above, starting with chloromethylated
Amberlite™ macroporous resin (4 percent crosslinked, 20 to 50 mesh, 4.3
meq Cl/g).

   F.   PREPARATION OF CATALYST FROM MERRIFIELD® RESIN AND 1,3-
PROPANESULTONE (PMPSA-MER)

        Catalyst was prepared above, by treating Merrifield® resin (2
percent crosslinked, 200 to 400 mesh, 4.3 meq Cl/g) with lithiated 1,3-

propanesultone, which can be prepared in accordance with T. Durst et al.,
"A new route to 5- and 6-membered ring sultones", Can. J. Chem., Volume 48
(1970), Pages 845-851.

EXAMPLE 10

5   EVALUATION OF A MERCAPTOSULFONIC ACID POLYMER (PMBSA) IN THE REACTION OF
PHENOL WITH FLUORENONE

        A.   To a 4-dram vial equipped with a stirring bar (reactor design
2) was added 4.33 g of a 20.8:1 mole ratio mixture of phenol to fluorenone
and 0.26 g [(6 percent by weight of the reactant solution)] of the
10   mercaptosulfonic acid polymer (PMBSA) prepared as in Example 9B. The
reaction mixture consisted of a homogeneous liquid phase plus a separate
heterogeneous polymer catalyst phase. The mixture was heated to 36°C for 3
hours. To increase the rate of reaction, the temperature was increased to
50°C for 18 hours. Monitoring of the reaction by HPLC shows some reaction
15   at 36°C and 100 percent conversion after 18 hours at 50°C. HPLC analysis
(analytical method 2) gives the following relative area percent analysis
for the products after 18 hours of reaction (100 percent conversion):

% by area	product
98.86	BHPF
0.98	2,4-isomer
0.16	two:three adduct

        B.   (Comparative Example) DOWEX™ 50WX4 (a crosslinked sulfonated
polystyrene resin, from The Dow Chemical Company) promoted with
2,2-dimethylthiazolidine (25 percent of the resin sulfonic acid
25   equivalents) was washed on a glass filter frit with phenol at 55°C to
remove water. The resin was then washed with a mixture consisting of a
20.8:1 mole ratio mixture of phenol to fluorenone at 55°C to displace the
original phenol wash. To a 4-dram vial equipped with a stirring bar
(reactor design 2) was added 2.13 g of a 20.8:1 mole ratio mixture of
30   phenol to fluorenone and 0.74 g (35 percent by weight of the reactant
solution) of the promoted DOWEX™ 50WX4, from The Dow Chemical Company,
catalyst activated as described above. The weight of catalyst used was
determined after the reaction by recovery of the resin from the reaction
mixture by filtration, washing the resin with toluene and hexane, and
35   drying to a constant weight in a vacuum oven at 50°C for 6 hours.

        The reaction mixture consisted of a homogeneous liquid phase plus a
separate heterogeneous polymer catalyst phase. The mixture was heated to

50°C for 18 hours. Monitoring of the reaction by HPLC showed approximately
17 percent conversion after 4 hours and 73 percent conversion after 18
hours at 50°C. HPLC analysis (analytical method 2) and gave the following
relative area percent analysis for the products after 18 hours of reaction

5   (73 percent conversion):

% by area	product
91.32	BHPF
6.78	2,4-isomer
1.90	two:three adduct

10   C.   (Comparative Example) To a 4-dram vial equipped with a
stirring bar (reactor design 2) was added 2.16 grams of a 20.8 : 1 mole
ratio mixture of phenol to fluorenone and 0.34 g (16 percent by weight of
the reactant solution) of dry Amberlyst™ 15 (a crosslinked sulfonated
polystyrene resin from Rohm and Haas Company). The reaction mixture

15 consisted of a homogeneous liquid phase plus a separate heterogeneous
polymer catalyst phase. The mixture was heated to 50°C for 18 hours.
Monitoring of the reaction by HPLC showed approximately 24 percent
conversion after 4 hours and 64 percent conversion after 18 hours at 50°C.
HPLC analysis (analytical method 2)and gave the following relative area

20 percent analysis for the products after 18 hours of reaction (64 percent
conversion):

% by area	product
95.82	BHPF
3.93	2,4-isomer
25 | 0.25 | two:three adduct |

        These experiments showed that use of the catalysts disclosed herein
gave higher conversions of fluorenone and higher 4,4/2,4-isomer ratios
than the prior art catalysts.

EXAMPLE 11

30 RECOVERY AND RECYCLING OF SOLID CATALYST (PMBSA)

        A.   CATALYST RECOVERY

The reaction mixture from Example 10A was cooled to 40°C and the mixture
was centrifuged. The upper liquid layer was decanted and additional warm
(40 to 45°C) 20.8:1 mole ratio phenol/fluorenone solution (approximately 3

35 to 4 times the catalyst volume) was added. The mixture was stirred,
centrifuged, and the warmed liquid layer was decanted. This wash
procedure was repeated for a total of three washes, then the required

-65-

amount of phenol/fluorenone reactant mixture was added and the reaction began.

B.   FIRST RECYCLE

To the 4-dram vial containing the mercaptosulfonic acid polymer recovered (as described above) from Example 11A was added 4.33 grams of a 20.8:1 mole ratio mixture of phenol to fluorenone. The mixture was heated to 50°C for 4 hours. Monitoring of the reaction by HPLC showed approximately 90 percent conversion after 4 hours at 50°C. HPLC analysis (analytical method 2) and gave the following relative area percent analysis for the products after 4 hours of reaction (90 percent conversion):

% by area	product
98.77	BHPF
1.09	2,4-isomer
0.14	two:three adduct

C.   SECOND RECYCLE

To the 4-dram vial containing the mercaptosulfonic acid polymer recovered (as described above) from the first recycle was added 4.00 grams of a 20.8:1 mole ratio mixture of phenol to fluorenone. The mixture was heated to 50°C for 18 hours. Monitoring of the reaction by HPLC shows approximately 83 percent conversion after 4 hours and 100 percent conversion after 18 hours at 50°C. HPLC analysis (analytical method 2) gives the following relative area percent analysis for the products after 18 hours of reaction (100 percent conversion):

% by area	product
98.79	BHPF
1.10	2,4-isomer
0.11	two:three adduct

D.   THIRD RECYCLE

To the 4-dram vial containing the mercaptosulfonic acid polymer recovered (as described above) from the second recycle added 2.00 grams of a 20.8:1 mole ratio mixture of phenol to fluorenone. The mixture was heated to 40°C for 18 hours. Monitoring of the reaction by HPLC shows approximately 90 percent conversion after 4.5 hours and 100 percent conversion after 18 hours at 40°C. HPLC analysis (analytical method 2)

gives the following relative area percent analysis for the products after
18 hours of reaction (100 percent conversion):

% of area	product
99.08	BHPF
0.92	2,4-isomer
*	two:three adduct
*	not detectable

These experiments showed that the catalyst can be recycled
repeatedly without loss of activity.

10   EXAMPLE 12

COMPOSITE EXPERIMENTAL DETERMINATION OF PARAMETERS FOR THE CONDENSATION OF
PHENOL WITH FLUORENONE (3-MPSA, DIPHENYL-METHANE)

Experiments were run in stirred isothermal batch reactors (reactor
designs 2 or 3) to determine the effect of temperature, molar ratios of
15   reactants and amount of MPSA on reaction rates and product distribution.
Results were shown in Table I.

Graphical analysis of the results in Table I shows that formation of
2,4-BHPF was related to the reaction temperature. As the temperature
increased, the 2,4/4,4 ratio increases. In contrast, the phenol/Fn mole
20   ratio has little effect on the 2,4/4,4 ratio. The yield of 2:3 adduct
increases markedly as the ratio of phenol/Fn decreases from 15:1 to 2.5:1
and the reaction temperatures was increased from 25°C to 85°C.

Graphical analysis of results for runs at 18 mole percent of MPSA,
in terms of initial reaction rates (BHPF moles/L*hr) showed a marked rate
25   increase in going from 25°C to 85°C.

Increasing the concentration of MPSA catalyst also gives the
expected increase in the reaction rate. The phenol:fluorenone ratio also
affects the reaction rate. It was believed that higher ratios of phenol
to fluorenone were beneficial for condensations, run in a solvent, such as
30   diphenylmethane.

TABLE I

PHENOL + Fn -----> BHPF

Catalyst MPSA, 10% Fn in DPM

5

Analytical Method 2 - UV Detector

Run #	Temp. (°C)	Mole Ratio	Mole% MPSA	2,4/4,4 Area	2:3/4,4 Area	Conv. (%)	Initial Rates*
1	55	8.62	12.8	0.0261	0.0198	99	0.16
2	25	2.46	7.9			14	0.0002
3	85	2.46	7.9	0.0389	0.114	62	0.047
4	25	14.75	7.9			12	0.028
5	85	14.75	7.9	0.0299	0.0098	99	0.53
6	25	2.46	17.7			5	0.001
7	85	2.46	17.7	0.0334	0.102	67	0.59
8	25	14.75	17.7	0.0202	0.0074	99	0.041
9	85	14.75	17.7	0.0317	0.0106	99	0.88
10	25	8.62	12.8	0.0239	0.0179	99	0.0042
11	85	8.62	12.8	0.0354	0.0244	99	0.73
12	55	2.46	12.8	0.0252	0.0673	57	0.035
13	55	14.75	12.8	0.0237	0.0076	99	0.17
14	55	8.62	7.9	0.0264	0.0177	99	0.12
15	55	8.62	17.7	0.0291	0.0248	99	0.42
16	55	8.62	12.8	0.0285	0.0185	99	0.15
17	63	14.75	12.8	0.026	0.00911	99	
18	63	14.75	12.8	0.0259	0.0088	99	
19	63	14.75	12.8	0.026	0.0088	99	
20	63	14.75	12.8	0.0266	0.0084	99	0.29
21**	63	14.75	12.8	0.0272	0.0096	99	
22	63	14.75	12.8	0.0265	0.0098	98	
23	63	14.75	12.8	0.0269	0.0092	98	
24	55	14.75	17.7	0.0255	0.0084	98	0.36
25	55	2.46	17.7	-	-	24	0.14
26	63	9.9	5	0.0258	0.015	98	0.078
27	25	14.75	12.8	0.0178	0.0067	98	0.013

35

Footnotes to Table I:
    BF = BHPF (4,4-isomer)
    2:3 = two:three adduct
    *BHPF moles/L hr.
    ** recycle

TABLE II

PHENOL + Fn -----> BHPF

Catalyst MPSA, Various % Fn in Solvents

Analytical Method 2 - UV Detector

Run	Temp °C	Solvent	% Fn*	Mole Ratio	Mole% MPSA	2,4/4,4 Area	2:3/4,4 Area	Time hr	% Conv
1	65	DPM	21	10	18	0.029	0.017	2	98
2	55	DPM	55	15	6.5	0.012	0.008	4	100
3	33	DPM	38.4	30	11.5	0.013	0.005	2.5	95
4	45	DPM	55	20.8	14.6	0.016	0.006	2	100
5	45	DPM	55	15	5.0	0.013	0.005	6	100
1A	27	DPM/MC	29	21	4.6	0.010	0.005	19.5	100
2A	35	MBenzoate	-55	21	8	0.015	0.004	6.5	86
3A	35	ClBenzene	13	21	25.6	0.018	0.005	3.25	99
4A	35	2,4,6TMPh	14	21	14.6	0.014	0.002	3	38

*In solvent

DPM = diphenylmethane

DPM/MC = diphenylmethane + methylene chloride

MBenzoate = methyl benzoate

ClBenzene = chlorobenzene

2,4,6TMPh = 2,4,6-TrimethylPhenol

The results in Table I showed that the 2,4/4,4 ratio stays constant as conversion increases, whereas the 2:3/4,4 ratio increases.

The amount of MPSA catalyst were related to the amount of 2,4-isomeric product formed. High 2,4/4,4 ratios at high concentrations of MPSA were probably related to a shift toward an acid-catalyzed reaction to produce relatively higher amounts of 2,4-isomer.

EXAMPLE 13

EFFECTS OF SOLVENTS ON PRODUCT DISTRIBUTION AND CONVERSIONS

Experiments were run in stirred tank batch reactors to determine whether use of a solvent was advantageous. Results of these experiments were shown in Table II. The use of a solvent does not appear to be advantageous. Comparison of a run using 10 percent DPM with neat run, at the same MPSA concentration, showed that reaction rates were higher for the neat run, although the DPM run uses 2.5 times more catalyst/Fn.

Higher 2,4/4,4 and 2:3-adduct ratios for the reactions in DPM was another disadvantage. It was therefore preferred to run the condensations in excess phenol as solvent.

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EXAMPLE 14

EFFECTS OF TEMPERATURE, MPSA CONCENTRATION AND PHENOL/FLUORENONE RATIOS ON
PRODUCT DISTRIBUTIONS (EXCESS PHENOL AS SOLVENT)

Reactions were done in isothermal stirred tank reactors as described
5   above. Results were presented in Table III. These results demonstrate
that increasing the amount of catalyst increased the 2,4/4,4 isomer ratio.
Increasing the reaction temperature or decreasing the phenol/Fn mole ratio
leads to higher amounts of 2:3 adduct in the product mixture.

EXAMPLE 15

10 RECOVERY AND RECYCLING OF MPSA FROM THE REACTION MIXTURES

Runs of 100 mL to 1.5 L (reactor designs 3 and 4) were done to
determine whether MPSA can be extracted from the neat BHPF reaction
solution with water and recycled to subsequent runs. The effect of
stirrer rpm on the time required for breaking a resulting emulsion were
15 also investigated.

Phenol was weighed and charged into the reaction vessel. Fluorenone
was weighed and charged to the reaction vessel, followed by a weighed
quantity of MPSA catalyst.

TABLE III

PHENOL + Fn -----> BHPF

Catalyst MPSA, Neat Reactions - no solvent

Analytical Method 2 - UV Detector

Run #	Temp. (°C)	Mole Ratio	Mole % MPSA	Time (hr.)	2,4/4,4 Area	2:3/4,4% Area	% Conv.	MPSA **
1	65	10	5	2.2	0.017	0.011	99	0.0470
2	35	2	8	3	0.013	0.003	98	0.0382
3	55	21	8	1.5	0.016	0.004	100	0.0382
4	63	10	2	7.5	0.014	0.008	97	0.0187
5	63	15	13	1	0.017	0.005	-	0.0846
6	28	10	5	20	0.011	0.008	92	0.0470
7	45	10	5	5	0.012	0.007	91	0.0470
8[1]	36	21	8	5	0.013	0.005	62	
9	36	21	3.9	7.25	0.012	0.005	95	0.0191
10[2]	36	21	4	6.5	0.012	0.007	96	0.0202
11	35	21	159	1.83	0.028	0.011	100	0.6932
12*	45	15	5	2.5	0.013	0.006	99	0.0330
13	45	15	5	3.5	0.014	0.007	100	0.0330
14*	55	21	3	2	0.014	0.006	99	0.0146
15[3]	35	21	18 mpa / 5.2 msa	20	0.034	0.011	100	0.0580

* = vacuum used to remove water during reaction.

** moles/L

---

[1] Molecular sieves used to remove water while reaction was taking place + more catalyst was added.

[2] Fn added continuously over 43 min.

[3] MSA (methanesulfonic acid) and MPA (mercaptopropionic acid) used instead of MPSA

The concentrations of materials in the resulting mixtures were followed by HPLC (Analytical Method 4).

The following mixtures were used:

	Neat Runs		DPM Runs	
Chem.	wt% theory	Chem.	wt% theory
Phenol	82.35	Phenol	47
Fn	0.00	Fn	0.00
MPSA	0.50	MPSA	0.21
H_2O	0.84	H_2O	0.48
BHPF	16.31	BHPF	9.3
		DPM	43

To the reactor was added 200 mL of the mixture and 200 mL of water. The resulting mixture was stirred for 10 minutes. The phases were allowed to separate and the separation time noted. A sample (10 mL) of the organic phase was removed for analysis by HPLC and I. C. (ion chromatography). The aqueous phase was retained for analysis.

The extraction of the remaining organic layer was repeated, using an equal volume of water (190 mL). At the end of the extraction and separation, 10 mL of the organic layer was retained.

The remaining 180 mL of organic layer was extracted with 180 mL of water. A 10-mL sample of the organic layer was retained, as before.

The aqueous extract was distilled under vacuum to give a solution of phenol, MPSA and small amounts of BHPF. Acid titration and I.C. analysis indicated that all of the MPSA was recovered from the mixtures. Results of representative extractions were given in Table IV.

Table IV
Extraction Data for Neat 21:1 (Phenol/Fn) Run
(500 rpm Stirring Rate)

Extraction	1		2		3	
Phase	Org.	Aq.	Org.	Aq.	Org.	Aq.
g. used	217	200	251.4	190	216.2	180
g. end	262.2	154.9	226.9	214.5	196.4	199.8

% Component in Phase

Phenol	62.8	6.71	57.6	6.63	59.2	6.39
Fn	0.00	0.0	0.00	0.0	0.00	
MPSA	0.08	0.55	0.030	0.12	0.0100	0.039
H_2O	23.7	92.7	28.0	93.3	25.1	93.6
BHPF	13.4	0.0098	14.4		15.8	0.0073

(150 rpm Stirring Rate)

Extraction	1		2		3	
Phase	Org.	Aq.	Org.	Aq.	Org.	Aq.
g. used	217	200	258	190	226.4	180
g. end	268.6	148.4	237.2	200.5	195.36	200.6

% Component in Phase

Phenol	60.1	6.37	61.6	7.17	61.1	6.82
Fn	0.00	0.0	0.00	0.0	0.00	
MPSA	0.10	0.53	0.0270	0.10	-0.005	0.03
P-1 H_2O	27.1	93.1	24.2	92.7	23.5	93.2
P-2 BHPF	12.7	0.0088	14.3	-	15.4	-

** 4th and 5th extractions: equal volumes of organic and water layers: MPSA in organic 0.0030 (4th), 0.0005 (5th), in water 0.0143 (4th), 0.0025 (5th)

EXAMPLE 16

ISOMERIZATION STUDY IN THE PRESENCE OF MPSA

Reactions were done in stirred batch isothermal reactors (reactor design 2). To the reactor was charged a mixture of 83.2 percent by weight of phenol, 0.09 percent by weight of fluorenone, 13.2 percent by weight of BHPF, containing 0.92 percent by weight of 2,4-isomer and 0.68 percent by weight of 2:3 adduct. Various amounts of MPSA were charged to the reactor. The resulting mixtures were stirred and heated. The compositions in the reactor at various times were determined by analytical method 4.

Compositions of other reaction mixtures were given in Table V. Results were given in Table VI.

These results showed that heating mixtures, in the presence of MPSA, brings about isomerization of the reaction mixtures toward higher concentrations of 9,9-bis-(4-hydroxyphenyl)-fluorene. The concentration of higher adducts also increases as a result of prolonged heating.

5

TABLE V

COMPOSITIONS FOR ISOMERIZATION STUDY

	Run	Temp °C	mole/L MPSA	mole/L Phenol	g Rx Mix	g MPSA
10	1	70	0.642	9.250	5.42	0.5710
	2	55	0.340	9.705	5.42	0.2878
	4	55	0.920	8.835	5.42	0.8540
	6	55	0.642	9.250	5.42	0.5710
	8	70	0.340	9.705	5.42	0.2878
15	9	70	0.920	8.835	5.42	0.8540
	15	55	0.180	9.940	5.42	0.1520

TABLE VI

ISOMERIZATION STUDIES

	Time	Phenol	Fn	% in Reaction Mixture			2nd add.*	% Total[+]	Total*
				BHPF	2:4*	2:3*			
Run 1	0	75.27	0.08	11.94	1.74	0.62	0.00	89.6	99.2
S#1	4	76.86	0.00	13.09	1.61	0.26	0.018	91.8	101.4
S#2	22.5	74.64	0.00	14.05	1.01	0.17	0.15	90.0	99.5
S#3	52	76.18	0.00	14.30	0.88	0.14	0.23	91.71	01.3
Run 2	0	79.00	0.09	12.66	1.84	0.65	0.00	94.2	99.3
S#1	4	81.9	0.0	13.1	1.9	0.5	0.00	97.4	102.5
S#2	21	76.71	0.00	13.21	1.56	0.29	0.0242	91.76	96.8
S#3	29	80.41	0.00	14.07	1.53	0.23	0.0169	96.25	101.3
S#4	94	80.96	0.00	14.18	0.89	0.14	0.07	92.17	101.2
S#5	101	77.22	0.00	14.62	0.94	0.21	0.10	92.99	98.0
Run 4	0	71.88	0.08	11.52	1.66	0.59	0.00	85.7	99.3
S#1	2	67.53	0.06	12.25	1.68	0.40	0.00	81.92	95.5
S#2	4.5	69.3	0.0	12.2	1.5	0.3	0.013	83.3	96.9
S#3	24.5	74.49	0.07	13.18	0.95	0.15	0.04	88.88	102.5
S#4	88	67.54	0.00	13.95	0.70	0.11	0.22	82.29	95.9
Run 6	0	76.02	0.08	12.06	1.75	0.62	0.00	90.5	100.1
S#1	2	73.72	0.00	13.01	1.83	0.51	0.00	89.0	98.6
S#2	4.5	75.4	0.0	13.2	1.8	0.4	0.0.	90.8	100.3
S#3	24.5	78.39	0.00	13.36	1.17	0.18	0.02	93.13	102.7
S#4	88	74.06	0.00	14.99	0.76	0.10	0.12	89.90	99.4
Run 8	0	84.03	0.09	13.33	1.94	0.69	0.00	100.1	105.1
S#1	7	78.92	0.00	14.00	1.69	0.29	0.00	94.90	99.0
S#2	23	76.1	0.00	14.6	1.2	0.2	0.1	92.2	97.2
S#3	52	79.09	0.00	14.92	1.02	0.15	0.12	95.30	100.3
Run 9	0	72.59	0.08	11.52	1.68	0.59	0.00	86.5	100.1
S#1	3	68.42	0.00	12.90	1.31	0.20	0.03	82.87	96.5
S#2	7	70.5	0.0	13.2	1.0	0.2	0.1	84.8	98.4
S#3	22.5	70.86	0.00	12.99	0.76	0.16	0.19	84.95	98.6
Run 15	0	80.93	0.09	12.97	1.87	0.66	0.00	96.5	99.1
S#1	2	83.36	0.00	13.83	2.01	0.66	0.00	99.8	102.6

* estimated

+ including catalyst

EXAMPLE 17

PURIFICATION OF 9,9-BIS-(4-HYDROXYPHENYL)FLUORENONE

A.   PRECIPITATION FROM METHYLENE CHLORIDE

A synthetic reaction mixture (105.5 g: 63 percent by weight, 66.5 g of phenol; 20 percent by weight, 21.1 g of 4,4-BHPF and 17 percent by weight, 18 g of water) was placed in a 500-mL round-bottom three-neck flask equipped with a heating mantle/Variac, thermometer, stirring bar and distillation arm. A "Therm-O-Watch" was used to control temperature of the liquid in the flask. A separate thermometer was placed in the distillation tower to monitor temperature in the vapor phase.

The mixture was stirred and heated at ambient pressure up to a
temperature of 160°C, during which time distillation of phenol and water
occurred. Analysis of the reaction mixture indicates the phenol:BHPF mass
ratio was 1:1. The reaction mixture, while still hot, was slowly added to

5   176 g of BHPF-saturated methylene chloride and the resulting mixture was
slowly swirled to produce a homogeneous solution, clear and yellow in
color. The mixture was allowed to cool to room temperature which causes
crystallization to occur.

The rod-like crystals present in the magma were analyzed by

10   microscope prior to filtration. Approximately 80 percent of the crystals
viewed were longer than 100 microns and have a diameter between 20 and 50
microns.

The crystal magma was filtered on a medium porosity glass frit, using
a vacuum produced by water jet. The filter cake was displacement-washed

15   with 79 g of BHPF-saturated methylene chloride and then 72 g of hot (90°C)
water. After drying at 65°C in air overnight, 12.9 g of white product was
recovered. Isolated yield was 61 percent and HPLC purity was 99.8
percent.

B.   WASHING WITH SODIUM BICARBONATE SOLUTION

20   Synthetic reaction mixture (105.5 g as in Example 17A) was combined
with 100 mL of a 2 percent by weight aqueous solution of sodium
bicarbonate. The mixture was agitated and then the organic and aqueous
layers were allowed to separate in a separatory funnel. The organic layer
was drawn off. This process was performed a total of 4 times. Washed

25   reaction mixture (85.2 g: 58 percent, 58 g of phenol; 17.4 percent, 17 g
of 4,4-BHPF and 25 percent, 21 g of water) was placed in the apparatus,
described in Example 17A.

The mixture was stirred and heated at a pressure of 80 to 100 mm Hg,
up to a temperature of 160°C, during which time distillation of phenol and

30   water occurred. BHPF-saturated phenol (100 g) was then added to the
reaction mixture and the temperature of the mixture was controlled at 65°C.
Crystallization began within 1 hour. The slurry was stirred overnight,
after which the rod-like crystals present in the magma were analyzed by
microscope before filtration. Approximately 30 percent of the crystals

35   viewed have a length greater than 100 microns and a diameter between 10
and 30 microns.

The crystal magma was filtered on a medium porosity glass frit using a vacuum produced by a water jet. The brown filter cake was displacement-washed with 200 mL of room-temperature water and then stir-washed with the same amount of water. The brown/beige crystals were then

5   washed with BHPF-saturated methylene chloride and then with ethylene dichloride. After drying at 65°C in air overnight, 7 g of brown product were recovered. The isolated yield was 47 percent and HPLC purity was 99.7 percent.

C.   DISTILLATION OF PHENOL, CRYSTALLIZATION FROM TOLUENE

10   Synthetic reaction mixture (149 g: 17.5 percent by weight, 24 g of 4,4-BHPF; 95 g of phenol and 30 g of water) were charged to the reactor, described in Example 17A. The mixture was stirred and heated at a pressure of 80 to 100 mm Hg up to a temperature of 160°C, during which time distillation of phenol and water occurred until the phenol:BHPF mass ratio

15   was reduced to approximately 1:1. There was no increase in adduct concentration.

The resulting mixture was added while still hot, to 121 g of BHPF-saturated toluene. The resulting homogeneous solution was allowed to cool to room temperature, during which crystallization occurred. The resulting

20   rod-like crystals present in the magma were analyzed by microscope prior to filtration. Approximately 20 percent of the crystals viewed had a length greater than 100 microns and a diameter between 10 and 50 microns.

The crystal magma was filtered on a medium porosity glass frit using a vacuum produced by a water jet. The pink filter cake was treated

25   similarly to other examples. After drying at 65°C in air overnight, 18.5 g of pink product were recovered. Isolated yield was 77 percent and HPLC purity was 98.1 percent.

D.   DISTILLATION OF PHENOL; CRYSTALLIZATION FROM METHYLENE CHLORIDE

30   Phenol and fluorenone were combined in the presence of 3-mercaptopropanesulfonic acid (MPSA) to produce a reaction mixture which, after washing to remove the acid catalyst, contained 20 weight percent of 4,4-BHPF, 64 weight percent of phenol and 16 weight percent water. The reaction mixture was distilled under water jet vacuum (approximated 80 mm

35   Hg) up to a temperature of 160°C to yield a residue, containing approximately 50 weight percent of phenol and 50 weight percent of 4,4-BHPF, that is, a 1:1 phenol:4,4-BHPF mass ratio.

The 1:1 mixture was cooled to 120°C and then poured into 176 g of room temperature methylene chloride, that had been previously saturated with 4,4-BHPF. This results in a clear homogeneous solution at reflux, which was allowed to cool to room temperature. The crystallized mixture
5   was filtered under vacuum at room temperature. The filter cake was displacement washed with 79 g of BHPF-saturated methylene chloride (no stirring of the filter cake during the wash) and then stir-washed with 72 g of hot water (90°C). The resulting white filter cake was dried in air at 60°C to provide a yield of 61 weight percent of the 4,4-BHPF originally
10   detected in the reaction mixture.

E.   REMOVAL OF PHENOL-WATER AZEOTROPE

Approximately 380 g of a reaction mixture similar to that of Example 17D were slowly dripped into 4 L of water at a temperature of 84°C at a pressure of 300 mm Hg. This dilution in water was accompanied by the
15   removal of phenol in the form of a water/phenol azeotrope. The water-insoluble materials then precipitate from the liquid phase as a white powder. Approximately 64 g of "crude" BHPF was obtained in this manner. The "crude" BHPF contained all the impurities originally contained in the reaction mixture. The product was filtered, washed with boiling water and
20   dried in air at 60°C to provide a recovery of 96 weight percent of the 4,4-BHPF originally detected in the reaction mixture.

F.   CRYSTALLIZATION FROM TRIISOPROPYLBENZENE

A reaction mixture (55.8 g: 63.1 percent by weight, 35 g of phenol; 14 percent by weight of 4,4-BHPF and 23 percent by weight, 12.8 g of
25   water) was charged to a 250-mL round bottom flask, otherwise fitted out as in Example 17A. Triisopropylbenzene (TIPB, 106.6 g) was added to the mixture in the flask, as a result of which the mixture separates into two phases, of which the yellow reaction mixture was the lower.

The mixture was stirred and heated under vacuum, produced by a water
30   jet (ca. 80 mm). After removal of
water at 50 to 88°C, the mixture appeared homogeneous. The mixture was stirred and allowed to cool. Solids appear when the temperature reached 70°C. The mixture was allowed to cool to room temperature and filtered on a glass frit under vacuum. The white solids on the frit were washed with
35   TIPB. The filter cake was left overnight under vacuum (water jet) while air was pulled through the filter cake.

Analysis of the resulting mother liquor showed that little of the phenol in the feed was removed as a result of distillation. The filter cake contained 4.2 g of white, nearly free-flowing product (54 percent recovery, 98.8 percent purity by HPLC).

5   G.   DISTILLATION TO REMOVE PHENOL; CRYSTALLIZATION FROM METHYLENE CHLORIDE

A reaction mixture (98.8 g: 61 percent by weight, 60.3 g of phenol; 19.4 percent by weight, 19.2 g of 4,4-BHPF and 19.6 percent by weight, 19.4 g of water) was charged to an

10   apparatus, described in Example 17F. A collection flask was attached to the distillation arm and connected to a vacuum source (a water jet). The temperature set point was adjusted to 100°C and heating began.

Temp. (°C)	Observations/Actions
50-55	boiling and distillation occur
100	slight bubbling
	set point raised to 120°C
105	distillation restarts
115	insignificant distillation
	set point raised to 140°C
120	vigorous boiling, little distillation,
	vapor temperature rising
121	vigorous boiling, distillation starting,
	vapor temperature 115°C
122	vapor temperature 118°C
	break vacuum and remove sample: 34 g of distillate
	collected, mixture in pot has phenol:BHPF mass
	ratio of ca. 2:1
	reconnect vacuum source and recommence heating
124	vapor temperature was 119°C, distillation
	starts
125	vapor temperature was 119°C
	break vacuum and sample mixture
	13.9 g of distillate collected
	set point 120°C at atmospheric pressure
	reconnect vacuum and recommence heating
	phenol:BHPF 1.6:1 mass ratio in pot
129	vapor temperature 121°C
	distillation starts
131	vapor temperature 123°C
	stop operation, remove sample
	42.4 g remain in pot; mixture in pot has
	phenol:BHPF ratio ca. 1.12:1; 6.7 g of distillate
	collected

The pot residue at 110°C was added to 172 g of fresh drum-grade methylene chloride in a bottle. The addition was done slowly in order to avoid excessive flashing or boiling of the methylene chloride. The resulting mixture more or less separated into two layers, of which the

5   upper layer was richer in the phenol:BHPF component. The mixture was swirled and became homogeneous. The bottle was sealed and placed in a pan of cold water (approximately 10°C).

Time	Observations/Actions
(hr:min.)	
0:08	homogeneous yellow solution
0:18	homogeneous yellow solution
0:56	yellow solution, possibly small crystals
1:18	same
2:00	same
2:24	crystallization ongoing, quite a few crystals
17:48	solid yellow crystalline mass breaks up easily filter under vacuum through glass frit to obtain slightly yellow crystals; recover 158.8g of yellow mother liquors

10

15

20

The crystallizer bottle was rinsed with 29.7 g of fresh methylene chloride (not all solids dissolve), the resulting mixture being used to displacement wash the filter cake, which improved slightly in color.

The filter cake was slurry washed with 49.4 g of fresh methylene

25   chloride and the resulting slurry was filtered under vacuum. The color of the filter cake was unchanged.

The filter cake was displacement washed with 33 g of cold water, without a change in the color of the cake. The filter cake was slurry-washed with 40 g of boiling water, without a change in the color of the

30   cake.

The cake was dried in air under vacuum for approximately 2 hours, transferred to a watch glass and dried in an oven overnight at 65°C. The cake was slightly yellow.

The mass balance for the process was:

<u>g of BHPF</u>

    19.2 in initial mixture

    8.1 in mother liquors at end of operation

    9.1 isolated product

    1.7 in wash

    0.3 unaccounted for

H.   CRYSTALLIZATION FROM DIPHENYLMETHANE

1.   A mixture of 28 g of DPM, 17.5 g of phenol, 5.4 g of BHPF (98:2 4,4- to 2,4- isomers, by HPLC) and 12 mg of MPSA was washed with water. The resulting layers were separated and the water layer was removed. Phenol was distilled from the organic layer to give a mixture containing 21.8 g of DPM, 3.8 g of phenol and 5.4 g of BHPF. The mixture was to be cooled to room temperature to give an off-white precipitate, which was filtered and washed with DPM. The washed cake was dried in an oven at 60°C to give 6.1 g of material, containing 70 percent by weight of BHPF and 30 percent by weight of phenol. The mixture was stripped at 140°C under nitrogen at < 80 mm Hg to give 4.2 g of white solid. The solid, by HPLC analysis (analytical method 5), contained 99.6 percent by area of the 4,4-isomer and 0.04 percent by area of 2,4-isomer.

2.   A reaction mixture from 15:1 phenol:fluorenone, containing 34.5 percent by weight of phenol and 10.5 percent by weight of BHPF, was diluted with 55 percent by weight of DPM. Phenol (80 percent of that initially present, maximum temperature 105°C, 4.5 mm Hg) was removed by distillation to give, after crystallization from DPM, white BHPF melting at 221 to 222°C. The recovery of BHPF was 78 percent. The material contained 99.6 percent of the 4,4-isomer by HPLC.

I.   CRYSTALLIZATION FROM NEAT PHENOL

Phenol was distilled from the reaction mixtures to produce mixtures, containing less than 50:50 phenol:BHPF by weight. The resulting materials can be washed with methylene chloride. The products were inconsistent in color and contain small crystals, usually of the size of 10 to 70 microns.

J.   PRECIPITATION OF BHPF BY ADDITION TO WATER

Addition of reaction mixtures to boiling water or steam removed some phenol as a phenol-water azeotrope. The resulting product retained most of the extraneous isomers and adducts and comprised very small crystals,

the size of the order of 10 to 20 microns. The maximum purity was 97 to 98 percent.

Analytical data (HPLC) was given in Table VII for Samples, prepared in accordance with the practice of the invention and for commercially-available materials.

K.   REMOVAL AND RECOVERY OF PHENOL FROM BHPF REACTION MIXTURE

Excess phenol was removed from a reaction mixture to a 1:1 ratio of phenol:BHPF using a falling film evaporator. This was accomplished at 120° C/120 mm Hg. At this temperature, BHPF solubility in phenol was 45 percent.

After removing phenol, the BHPF-phenol mixture was kept at 90°C and stirred prior to addition of methylene chloride or other crystallizing solvent.

BHPF was crystallized at room temperature under a nitrogen pad. A batch crystallizer was cooled to 5 to 10°C for several hours during which BHPF crystallizes. Solid BHPF was separated from the resulting slurry using a batch pressure filter or basket filter. Optionally, a pressure filter can be used. Methylene chloride or other solvent can be recycled to the process.

BHPF crystals were dried under vacuum.

BHPF from Sloss (Birmingham, Alabama): The sample evaluated was a dry solid, from lot number 9307-03.

BHPF from Isonova (Austria): The sample evaluated was designated "Isonova 10/93".

BHPF from Rutgers-Nease (State College, Pennsylvania): The dry solid was from lot number 9306099.

BHPF from Isovolta (Neudorf, Austria): The sample, used as standard for the comparative studies, was received in 1988 and was designated "Isovolta 1988."

Analysis of the results in Table VII shows that 4,4-BHPF, purified by distillative removal of phenol:water azeotrope and extraction with methylene chloride, produces high purity BHPF.

TABLE VII

Sample Source	Lot No.	4,4-BHPF	2,4-BHPF	2:3 BHPF Add.	Other	Total Impur.
Sloss	9307-03	100	~0	0	0	0
Isonova	10/93	100	0	0		0.00
MeCl₂	Ex. 17D	99.94		0.06		0.06
Water ppt'd	Ex. 17E	97.59	1.87	0.40	0.14	2.41
Isovolta	1988	100	0	0		0
Rutgers Nease	93060099	99.28	0.58	0.14		0.72
DPM	Ex. 17H	99.6				

EXAMPLE 18

5   CORROSION STUDIES

A.   REACTION MIXTURES FOR BHPF PROCESS

Corrosion tests were performed using a representative reaction
mixture for the condensation of phenol with fluorenone using various
catalysts. The tests were done using metal specimens 3.81 cm in length,
10   1.59 cm in width, 0.32 cm thick, and having a 0.64 cm hole centered in one
end. The specimens were isolated from each other and the mounting rack
using polytetrafluoroethylene shoulder washers. The specimens were
exposed to both the liquid and vapor phases of each test cell. The
contents of the cells were stirred continuously and were maintained at the
15   selected temperature using YSI temperature controllers and GLASCOL™
heating mantles. The tests were run under a nitrogen pad. The chloride
content of the test mixtures was <500 ppm. The tests were run at 65°C for
13 days (312 hours). Compositions tested and results are presented in
Table VIII.

20   Results in Table VIII demonstrate that the reaction mixtures used
were considerably less corrosive than conventionally used reaction
mixtures.

TABLE VIII

CORROSION TESTING FOR BHPF REACTION MIXTURES

A. Reactor Mixture: 90.2 percent of Phenol, 8.3 percent of Fluorenone, 1.5 percent of MPSA (by weight)

Corrosion Rate (mpy)*

Metal	Liquid	Vapor	Remarks
316L ss**	nil***	< 0.1	uniform corrosion
904L ss	nil	0.1	uniform corrosion
2205 ss	nil	< 0.1	uniform corrosion
254 SMO ss	nil	nil	uniform corrosion

B. Water Extraction Mixture: 8.0 percent of Phenol, 91 percent of Water and 1.0 percent of MPSA (by weight)

Corrosion Rate (mpy)

Metal	Liquid	Vapor	Remarks
316L ss	0.1	0.1	uniform corrosion
904L ss	< 0.1	< 0.1	uniform corrosion
2205 ss	< 0.1	< 0.1	uniform corrosion
254 SMO ss	< 0.1	< 0.1	uniform corrosion

C. Recycle Concentrate: 29.87 percent of Phenol, 69.23 percent of Water and 0.9 percent of MPSA (by weight)

Corrosion Rate (mpy)

Metal	Liquid	Vapor	Remarks
316L ss	0.1	0.1	uniform corrosion
904L ss	< 0.1	< 0.1	uniform corrosion
Inconel 625	< 0.1	< 0.1	uniform corrosion
Hastelloy C-27	0.1	< 0.1	uniform corrosion
Hastelloy G-30	< 0.1	< 0.1	uniform corrosion

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* mpy = mils per year; 1 mpy = 0.00254 cm/yr

** ss = stainless steel

*** nil = < 0.01 mpy

B.   REACTION MIXTURES FOR BISPHENOL A PROCESS

A mixture containing 94.35 percent by weight of phenol, 4.15 percent by weight of acetone and 1.50 percent of MPSA was evaluated as in Example 18A.

5   The following results were obtained:

Corrosion Rate

Metal	Liquid	Vapor		
304L ss	pass	pass		pass =
316L ss	pass	pass	< 0.00254 cm/year	
904L ss	pass	pass		
2205 ss	pass	pass		
825 Ni	pass	pass		

The corrosion rates in both the liquid and vapor phases was < 0.00254 cm/year. The corrosion was uniform. The rate of corrosion was below that for conventional reaction mixtures for making bisphenol A.

15   EXAMPLE 19

A.   PREPARATION OF BISPHENOL A USING PMBSA

Bisphenol A was prepared from 14:1 phenol:acetone (mole ratio) at 50° C, containing the indicated amounts of solid catalyst. The product distribution was determined by analytical method 2.

20   The PMBSA catalyst of Example 9B, at a level of 6 percent by weight, gives 75 percent conversion after 5 hours. The product contained 99.0:1.0 of 4,4:2,4-isomers (area percent).

The PMBSA was recovered and reused in a second cycle. The conversion

25   after 4 hours was 60 percent. The product contained 99.1:0.9 of 4,4:2,4-isomers (area percent).

DOWEX™ 50WX4, from The Dow Chemical Company, (35 percent by weight as dry mass), promoted with 25 percent by weight of 2,2-dimethylthiazolidine, was used in a similar experiment. The conversion

30   after 4 hours was 43 percent and the product contained 98.0:2.0 (as area percent) of 4,4:2.4-isomers.

These experiments showed that a polymer-supported catalyst of this invention gave higher conversions and a higher yield of 4,4-isomer than a representative prior art catalyst.

35   B.   REACTION USING PMBSA IN A DOWNFLOW CONTINUOUS REACTOR

The reactor comprised a vertical tube. The bottom part of the tube was filled with glass beads, on top of which was provided a bed of PMBSA

catalyst resin. The remainder of the tube was filled with glass beads.
The tube was fitted with a pressure gauge, a pressure regulator, heating
means external to the catalyst bed and feed means at the bottom of the
tubular reactor for introducing the phenol and fluorenone reactants. The
5   feed was prepared in a container, provided with a nitrogen stream and
heated externally by a fluid. A valve was intermediate the feed
preparation container and a pump for introducing the feed into the bottom
of the reactor. A relief valve was placed between the pump and the
reactor.

10   The feed was introduced into the reactor at a predetermined rate and
passes upwardly through the lower bed of glass beads, which functioned as
a pre-heater, through the catalyst bed and the upper bed of glass beads,
whereupon the product was removed from the top part of the reactor for
analysis or further processing.

15   Experiments using 21:1 phenol:fluorenone and PMBSA catalyst gave the
following results as a function of flow rate and reaction temperature:

		49°C	69°C
Conversion (%)		80	100
BHPF in phenol (%)		14	16
Productivity (g BHPF/g cat/h)		0.57	0.44
Selectivity (% 4,4-BHPF)		98[+]	97[+]
Flow rate (g feed/g cat·h)	4.39	2.71	

These experiments showed that lower reaction temperatures favored
productivity and selectivity toward 4,4-BHPF, accompanied by decreased
25   conversion.

        C. CONVERSION OF ACETONE AS A FUNCTION OF REACTION TEMPERATURE

        Phenol-acetone mixtures (6 percent by weight acetone) were converted
to bisphenol A, using MPSA as catalyst in batch reactors. The following
results were obtained (Table IX):

TABLE IX

Acetone Conversion

Time (min)	25°C*	35°C*	55°C+	65°C	75°C+
0	0	0.10	0.22	0.25	0.26
20			0.40	0.48	0.49
25	0.04	0.42			
40			0.59	0.62	0.67
48			0.65	0.69	0.77
60	0.06	0.56	0.69	0.75	
72					0.82
90	0.09		0.79	0.85	0.89
120	0.13	0.72	0.83	0.89	0.94
180	0.20	0.80		0.95	0.96
240	0.26			0.97	
300				0.98	
360	0.32				0.99

*   mixture contained 2.2% by weight of MPSA and 2-3% by weight of water

+   mixture contained 1.3% by weight of MPSA and no added water

D.   REMOVAL OF MPSA CATALYST USING ION-EXCHANGE RESIN; PURIFICATION OF CRYSTALLINE BISPHENOL A

Condensation of phenol with acetone (4 percent by weight), containing 2 by weight of water, using 2.5 percent by weight of MPSA, was done at 35°C in plug flow mode, with a 3-hour residence time. Crystallization of bisphenol A occurred in the reactor. The crystals were isolated by filtration and residual acetone in the mother liquors was recycled to the process at 50°C. THE mother liquors were dried at 50°C (20 mm Hg) and the cycle was repeated after addition of make-up feed. About 90 percent of the acetone was converted to bisphenol A per pass.

Catalyst was removed from the product by first melting the crystals and washing the resulting oil with water, and then extracting the organic layer with water, which reduces the acid concentration below 100 ppm after three equilibrium stages. The remaining catalyst was removed using an anion exchange bed (<50 ppm, the limit of detection).

Bisphenol A, isolated by a single crystallization step, was of higher purity than products, generally obtained using two crystallizations. Bisphenol A isolated by a single crystallization, contained a maximum of 1200 ppm of 2,4-bisphenol. The process of this

5 invention therefore simplifies the isolation of high purity of bisphenol A, uncontaminated by oily higher condensates.

EXAMPLE 20

SOLID CATALYST PREPARED FROM POLYSTYRENE BY ALKYLATION WITH ALLYL BROMIDE, SULFONATION AND THIOLATION

10   A.   Polystyrene (Amberlite® XE 305) was alkylated with allyl bromide in the presence of trifluoromethanesulfonic acid in 1,2-dichloropropane at 50°C, generally in accordance with Tomoi et al., "A Novel One-pot Synthesis of Spacer- modified Polymer Supports and Phase-transfer Catalytic Activity of Phosphonium Salts Bound to the Polymer

15 Supports", Reactive Polymers, Volume 3 (1985), pages 341-349, to produce a material having 2-bromo-1-methylethyl chains. This material was sulfonated, generally at the ortho-position with respect to the side chain, by treatment with chlorosulfonic acid. The resulting sulfonyl chloride was converted to a sodium salt by reaction with sodium

20 bicarbonate.   The material was converted to a corresponding thiol by reaction with sodium thioacetate and converted to a corresponding acid by acidic hydrolysis. Materials prepared correspond to 28 and 48 percent of alkylmercaptan functionality (XEMSA).

        B.   The thus-prepared polymers (XEMSA) were used at a level of 6

25 percent by weight for reaction between phenol and fluorenone (20.8:1 mole ratio) at 50°C. Product composition was determined by analytical method 3.

        The polymer containing 28 percent of alkylmercaptan functionality gives 75 percent conversion after 5 hours. The product distribution was 96.8:3.2 of 4,4:2,4-isomers (area percent).

30   The product containing 48 percent of alkylmercaptan functionality gives 15 percent conversion after 2 hours. The product distribution was 96.8:3.2 of 4,4:2,4-isomers (area percent).

EXAMPLE 21

IN SITU METHOD FOR PREPARING THE POLYMER-SUPPORTED MERCAPTOSULFONIC ACID
CATALYST (PMBSA CLASS):

    A.   SULTONE ALKYLATION

5   To a mixture of 1,4-butanesultone (30.0 g, 220.0 mmol, 1.00
equivalent) and poly(vinylbenzylchloride) (PVBC, 33.6 g, approximately 220
mmol, 1.00 equivalent) of chloromethyl groups) was added via a cannula dry
tetrahydrofuran (600 mL) under a nitrogen atmosphere. The mixture was
stirred at room temperature until a homogeneous solution was obtained.

10   The solution was then cooled to -78°C using a dry ice/acetone bath. n-
Butyllithium (2.5 molar in hexanes, 88.1 mL, 1.00 equivalent) was added
slowly dropwise to the -78°C solution of 1,4-butanesultone and
poly(vinylbenzylchloride) via an addition funnel over approximately 2.5
hours with vigorous stirring. A white solid begins to precipitate from

15   the reaction mixture as the n-butyllithium addition was begun, with
precipitation continuing throughout the n-butyllithium addition period.
By the end of the addition, a large amount of white solid has formed
within the reaction medium.

        The reaction mixture (slurry) was allowed to slowly warm to room

20   temperature in the cooling bath (over approximately 3 to 4 hours) and was
allowed to stir at room temperature overnight. The white precipitate
which has formed in the reaction mixture during the n-butyllithium
addition period remains insoluble as the mixture reaches room temperature.
The white (insoluble) solid was removed by vacuum filtration. The polymer

25   can be washed with water or water can be added to the THF/polymer slurry
prior to filtration. Addition of water sometimes results in increasing the
time required for filtration. The solid was slurry-washed with THF, then
with methanol and finally with methylene chloride (causing some
swelling). The solid was dried overnight in a vacuum oven to provide 53.4

30   g of a white solid sultone-functional polymer.

        B.   THIOLATION

        To the sultone-functional polymer from above (110.0 g from two
combined batches, approximately 0.440 mol of sultone) was added nitrogen-
saturated THF (500 mL). In a separate reactor, a solution of lithium

35   thioacetate was prepared by the dropwise addition of thiolacetic acid
(49.8 g, 0.650 mol) to a slurry of lithium carbonate (24.2 g, 0.330 mol)
in water (100 mL, nitrogen saturated). The lithium thioacetate solution

was added slowly via cannula to the polymer/THF slurry at such a rate that
the temperature does not rise above 35°C. The polymer swells substantially
during the lithium thioacetate addition. After the lithium thioacetate
addition was complete, an additional 350 mL of water (nitrogen saturated)

5   was added. The polymer swells to a volume of approximately 1 L. The
mixture was heated to 50°C, and was allowed to react overnight. The gel-
like polymer was then filtered using a coarse glass-fritted funnel. The
polymer was washed with water, then with methanol, then with methylene
chloride, and finally with additional water. The polymer slurry sometimes

10   filters very slowly during the filtration process. In this case, the
washing steps required approximately two days.

       After the washing steps, concentrated hydrochloric acid (300 mL,
approximately 37 percent by weight in water) was added to the polymer.
The polymer shrinks in volume and the HCl solution was easily removed by

15   filtration. More concentrated HCl (300 mL) was added to the filtered
solid, and the mixture was allowed to stand at room temperature over 2
days. The polymer was then washed extensively with dilute HCl solution,
followed by extensive water washes. The polymer was then washed with
methanol and finally with dichloromethane. Drying overnight in a vacuum

20   oven (60°C/full vacuum) provided the polymer-supported mercaptosulfonic
acid. The product was identified as PMBSA-SU.

       C.   CONVERSION OF CROSSLINKED POLYSTYRENE RESIN TO
MERCAPTOSULFONIC ACID POLYMER

       A commercially-available (Fluka Chimika) crosslinked

25   chloromethylated Merrifield® resin (2 percent divinylbenzene, 200 to 400
mesh, approximately 4.3 mmol Cl/g , 51.2 g, 1.0 equivalent) was reacted
with 1,4-butanesultone (1.05 equivalents) and n-butyllithium (1.0 equiva-
lent) according to the procedure described above to provide a sultone-
functional polymer (70.0 g). Subsequent thiolation of the sultone polymer

30   in a manner similar to that described above provided the corresponding
mercaptosulfonic acid polymer (79.0 g dry mass). This material was
identified as PMBSA-MER.

       In this reaction sequence, the lithium thioacetate reagent was
formed in situ by slowly adding solid lithium carbonate to a mixture of

35   the sultone polymer and thiolacetic acid in a 3:2 volume ratio of
nitrogen-saturated THF/water.

EXAMPLE 22

PREPARATION OF POLYMER-SUPPORTED MERCAPTOSULFONIC ACID CATALYST (XEMSA CLASS)

A.   ALKYLATION OF POLYSTYRENE

To Amberlite™ XE-305 (75.0 g, approximately 0.720 mol of styrene repeat units, 1.00 equivalent) was added 600 mL of 1,2-dichloropropane (PDC). The polymer was allowed to swell in the solvent overnight. 5-Bromo-1-pentene (75.3 g, 0.702 equivalent) and PDC (125 mL) were added to an addition funnel. The reactor contents (polymer slurry and 5-bromo-1-pentene solution) were evacuated and back-filled with nitrogen several times. Trifluoromethanesulfonic acid (20.0 g, 0.133 mol, 0.19 equivalent) was added to the polymer/PDC slurry. The slurry solution turned a dark amber color. The polymer slurry was heated to 45 to 50°C, and slow, dropwise addition of the 5-bromo-1-pentene solution was begun. The 5-bromo-1-pentene solution was added slowly over approximately 3 days to the stirred polymer slurry at 50°C. After the 5-bromo-1-pentene addition was complete, the reaction was allowed to stir an additional 1 day at 50°C. The polymer slurry was very dark-colored throughout the addition period.

The polymer slurry (very dark red-brown) was cooled to room temperature and filtered. The beads were washed extensively with dichloromethane (still dark colored beads) and then were washed extensively with water to remove most of the color. The beads were then washed with the following series of solvents: methanol, acetone, dichloromethane, acetone, and, finally, methanol. After drying in a vacuum oven at 60°C overnight, 96.46 g of nearly white bromoalkylated polymer beads were obtained. The mass uptake corresponded to a degree of functionalization (DF) of approximately 0.20.

B.   SULFONATION

To the dried bromoalkylated polymer beads prepared above (approximately 0.720 mol of styrene repeat units) was added 650 mL of dichloromethane under a nitrogen atmosphere. The polymer slurry was cooled to 0°C using an ice water bath. Chlorosulfonic acid (258.2 g, 2.22 mol, 3.08 equivalents) was added slowly dropwise to the polymer slurry at 0°C over 2 hours 40 minutes. The polymer beads turn copper-colored during the chlorosulfonic acid addition. After the addition was complete, the reaction mixture was allowed to slowly warm to room temperature within the water bath. The volume of the swollen polymer was approximately 500 to

600 mL within the reactor. After warming to room temperature, the polymer
slurry was allowed to stand overnight without stirring. The liquid layer
was then removed from the polymer using a small-bore cannula. The beads
were then washed several times with dichloromethane. (The liquid layer

5   and dichloromethane washes were slowly and carefully quenched in a
separate vessel using ice.) The polymer beads were then carefully
transferred to a fritted-glass funnel, and the polymer beads were quenched
by slow, careful addition of ice water.

      After washing the beads extensively with water, excess solid sodium

10   bicarbonate was slowly added to a suspension of the polymer beads in
water. The mixture was allowed to stand overnight at room temperature.
The polymer/sodium bicarbonate mixture was then heated to 50°C for 2 hours.
The polymer slurry was allowed to stand at room temperature for 6 days.
The polymer was light-colored and more highly swollen at this point. The

15   slurry was heated to 50°C and allowed to react overnight, giving a pH 4
solution of even more swollen polymer (approximately 600 to 700 mL
volume). Addition of a small amount of sodium bicarbonate gives a pH 7
solution.

      C.   THIOLATION

20   To the aqueous polymer bead slurry from above was added sodium
bicarbonate (60.5 g, 0.720 mol). The mixture was evacuated and back-
filled with nitrogen three times. Thiolacetic acid (41.1 g, 0.540 mol)
was added slowly dropwise over 1 hours 10 minutes to the polymer slurry at
room temperature. The mixture was slowly warmed to 80°C over several hours

25   and allowed to react at 80°C for 3 days. After cooling to 40°C, the
supernatant solution was removed using a small-bore cannula. The polymer
was washed several times with water, giving slightly off-white colored
polymer beads. Concentrated hydrochloric acid (250 mL) was added to the
polymer and the slurry was heated to 50°C for 3 hours. After cooling to

30   room temperature, the hydrochloric acid solution was removed using a
small-bore cannula. The polymer beads were then washed several times with
diluted hydrochloric acid and the beads were transferred to a fritted-
glass funnel. The beads were again washed repeatedly with diluted
hydrochloric acid followed by extensive washings with water, giving

35   slightly off-white water-swollen beads. (The water-swollen volume of the
polymer beads was approximately 900 mL.) The beads were washed with
methanol (methanol-swollen volume approximately 600 mL) and finally with

-93-

dichloromethane. After drying in a vacuum oven at 60°C overnight, the dark-colored beads had a dry volume of approximately 200 mL. This product was identified as XEMSA-5C.

D.   PREPARATION OF CATALYST FROM POLYSTYRENE AND 11-BROMO-1-
5 UNDECENE (XEMSA-11C)

Catalyst was prepared as above, starting with macroporous polystyrene (Amberlite™ XE-305) and 11-bromo-1-undecene.

EXAMPLE 23

EVALUATION OF POLYMERIC MERCAPTOSULFONIC ACID CATALYSTS

10   A.   EVALUATION OF THE MERCAPTOSULFONIC ACID POLYMER (XEMSA-5C) IN THE REACTION OF PHENOL WITH FLUORENONE

To a 4-dram vial equipped with a stirring bar was added 4.32 g of a 20.8:1 molar ratio mixture of phenol to fluorenone and 0.26 g (6 percent by weight of the reactant solution) of the mercaptosulfonic acid polymer

15 (XEMSA-5C) prepared as described in Example 22A-C. The reaction mixture consists of a homogeneous liquid phase plus a separate heterogeneous polymer catalyst phase. The mixture was heated to 50°C for 5 hours. The reaction was monitored throughout the reaction period by collecting samples and analyzing by HPLC. The 9-fluorenone was found to be 36

20 percent consumed within 2 hours and 76 percent consumed within 5 hours. HPLC analysis (analytical method 3) gives the following relative area percent analysis for the products after 5 hours of reaction (76 percent conversion): 9,9-bis-(4-hydroxyphenyl)fluorene (97.45 area percent) : 9-(2-hydroxyphenyl)-9-(4-hydroxyphenyl)fluorene (2.17 area percent) : adduct

25 containing two fluorene units and three phenolic units (0.39 area percent).

B.   EVALUATION OF THE MERCAPTOSULFONIC ACID POLYMER (XEMSA) IN THE REACTION OF PHENOL WITH FLUORENONE

To a 4-dram vial equipped with a stirring bar was added 4.32 g of a
30 20.8:1 molar ratio mixture of phenol to fluorenone and 0.26 g (6 percent by weight of the reactant solution) of the mercaptosulfonic acid polymer (XEMSA, degree of functionalization approximately 0.28 from bromoalkylation step) prepared as described in Example 20. The reaction mixture consisted of a homogeneous liquid phase plus a separate

35 heterogeneous polymer catalyst phase. The mixture was heated to 50°C for 5 hours. The reaction was monitored throughout the reaction period by collecting samples and analyzing by HPLC. The 9-fluorenone was found to

be 44 percent consumed within 2 hours and 75 percent consumed within 5
hours. HPLC analysis (analytical method 3) gives the following relative
area percent analysis for the products after 5 hours of reaction (75
percent conversion): 9,9-bis-(4-hydroxyphenyl)fluorene (96.10 area

5   percent): 9-(2-hydroxyphenyl)-9-(4-hydroxyphenyl)fluorene (3.52 area
percent): adduct containing two fluorene units and three phenolic units
(0.38 area percent).

     C.   EVALUATION OF MERCAPTOSULFONIC ACID POLYMER (PMBSA-MER) IN THE
REACTION OF PHENOL WITH FLUORENONE

10   To a 4-dram vial equipped with a stirring bar was added 4.32 g of a
20.8:1 molar ratio of phenol:fluorenone and 0.26 g (6 percent by weight of
the reaction solution) of PMBSA-MER of Example 21C. The reaction mixture
consists of a homogeneous liquid phase plus a separate heterogeneous
polymeric catalyst phase. The mixture was heated at 50°C for 2 hours. The

15   reaction was monitored by collecting samples, which were analyzed by HPLC.
The 9-fluorenone was 99.5 percent consumed within 2 hours. The product
after 2 hours contained 96.83 area percent of 9,9-bis-(4-
hydroxyphenyl)fluorene, 2.44 area percent of 9-(2-hydroxyphenyl)-9-(4-
hydroxyphenyl)fluorene and 0.72 area percent of an adduct containing two

20   fluorene units and three phenolic units by HPLC (analytical method 3).

     D.   EVALUATION OF MERCAPTOSULFONIC ACID POLYMER (PMBSA-SU) FOR THE
REACTION OF PHENOL WITH FLUORENONE

     To a 4-dram vial equipped with a stirring bar was added 4.32 g of a
20.8:1 molar ratio mixture of phenol:fluorenone and 0.26 g (6 percent by

25   weight of the reactant solution) of the polymer of Example 21B (PMBSA-SU).
The reaction mixture consisted of a homogeneous liquid phase plus a
separate heterogeneous polymer catalyst phase. The mixture was heated to
50°C for 5 hours. The progress of the reaction was followed by HPLC. At
the end of 2 hours, 67 percent of the fluorenone was consumed, and 85

30   percent at the end of 5 hours. At the end of 5 hours, the reaction
mixture contained 97.09 area percent of 9,9-bis-(4-hydroxyphenyl)fluorene,
2.25 area percent of 9-(2-hydroxyphenyl)-9-(4-hydroxyphenyl)fluorene and
0.66 area percent of an adduct containing two fluorene units and three
phenolic units by HPLC analysis.

35   Results for the evaluation of various polymer mercaptosulfonic acids
for condensing phenol with fluorenone were given in Table X.

<u>TABLE X</u>

<u>CONVERSION OF FLUORENONE (%) USING 6% BY WEIGHT OF POLYMERIC CATALYSTS AT</u>

<u>50°C</u>

				Reaction time (h)		
Resin	0	2	4	5	7	18
PMBSA-MER	0	99.5				
PMBSA-SU (PVBC)	0	67		85		
PMBSA (PVBC)	0	66				
XEMSA-5C (Amberlyte™ XE-305)	0	36		76		
XEMSA (Amberlyte™ XE-305)	0	49		75	82	
DOWEX* 50 (DMT promoted)	0		17			73

*Trademark of The Dow Chemical Company.

*Amberlyte™ Trademark of Rohm and Haas

<u>EXAMPLE 24</u>

EVALUATION OF THE MERCAPTOSULFONIC ACID POLYMERS IN THE REACTION OF PHENOL
WITH ACETONE

     To a 4-dram vial equipped with a stirring bar was added 4.33 g of a
14:1 molar ratio mixture of phenol to acetone and 0.26 g (6 percent by
weight of the reactant solution) of the appropriate mercaptosulfonic acid
polymer. The reaction mixture typically consists of a homogeneous liquid
phase plus a separate heterogeneous polymer catalyst phase. The mixture
was heated and allowed to react at 50°C. The reaction was monitored
throughout the reaction period by collecting samples and analyzing by
HPLC. HPLC analysis (analytical method 3) shows the following acetone
percent conversion data (based upon the quantity of bisphenol A produced)
for the different catalysts are given in Table XI:

TABLE XI

% ACETONE CONVERSION

(BASED UPON BISPHENOL A PRODUCED)

		Reaction time (h)				
Resin	0.0	1.0	2.25	2.5	4.0	5.0
DOWEX* 50WX4, 25% DMT promoted	0		18		44	
PMBSA (from uncrosslinked PVBC)	0		35		60	75
XEMSA-5C (DF ≈ 0.20)	0		38			82
XEMSA (DF ≈ 0.28)	0		23			32
PMBSA-SU	0	2		9		
PMBSA-MER (2% cross-linked, 200-400 mesh)	0	66		88		

*Trademark of The Dow Chemical Company

DMT was 2,2-dimethylthiazolidine

EXAMPLE 25

    A.   PREPARATION OF BHPF; METHYLENE CHLORIDE AZEOTROPE TO REMOVE
WATER; PRECIPITATION FROM METHYLENE CHLORIDE; 5.75:1 MOLAR RATIO OF PHENOL
TO 9-FLUORENONE; COPRECIPITATION WITH TETRACHLOROETHYLENE

    To a reactor (isothermal stirred batch reactor; reactor design 4) was
charged 75.0 g (0.80 mole) of phenol and 24.98 g (0.1386 mole) of 9-
fluorenone. The mixture was heated to 40°C and catalyst (0.973 g, 0.0062
mole, 3-mercaptopropanesulfonic acid) was charged to the reactor. Heating
was continued. The course of the reaction was followed by HPLC
(analytical method 3). At 30 percent conversion, methylene chloride (15
g) was added to the reaction mixture so as to keep the mixture stirred,
and to use a water/methylene chloride azeotrope (180 mm Hg, T = 37°C) to
remove water of reaction. The reaction mixture was cooled at the end of
the reaction (nearly complete fluorenone consumption, >99 percent of
theoretical water) to increase the amount of crystalline precipitate. The
progress of the run is given in Table XII.

    The reaction mixture (about 97 percent selectivity to 4,4-BHPF, little
unreacted fluorenone) was split into two parts. The first fraction (53.3
g) was filtered. The filter cake was washed with methylene chloride (49
g) and then with hot water (55 g). The recovery was 6.4 g (first crop)

and 0.6 g (second crop) of white crystals, corresponding to 99 percent
purity 4,4-BHPF (33 percent recovery).

   To the remainder of the mixture (70.3 g) was added 61 g of
tetrachloroethylene. The crystals were removed by filtration and the
5 filter cake was washed with 50 g of tetrachloroethylene and then with 115
g of hot water. The recovered product weighed 11.5 g (43 percent
recovery, 99 percent as 4,4-BHPF, white solid).

   These results showed that use of tetrachloroethylene, in combination
with methylene chloride, gives higher recovery of 99 percent pure 4,4-
10 BHPF).

<div align="center">TABLE XII</div>

Time h:min	Temp. °C	mm. Hg	Observations, Actions
0:0	37	760	Add MPSA; turns orange, then dark green brown
0:20	36	760	Color light brownish
0:40	36	760	Sample taken
1:15	36	760	Seed crystal added
2:10	36	760	Sample taken
2:28	36	760	Methylene chloride (15 g) and seed crystal added; no crystallization; temp. raised to 45°C
2:30	37	-180	Sample taken; seed crystal not dissolving
3:10	45	-180	Heater set at 40°C
3:30	40	-180	Seed crystals added
3:50	40	-180	Mixture hazy
4:30	40	-180	Mixture hazy
5:10	40	-180	Sample taken
6:43	40	760	Vacuum turned off, stirrer speed increased
9:30	40	760	Sample taken; methylene chloride (about 20 g) added to mixture; stirrer speed increased; heater turned off

B.   USE OF METHYLENE CHLORIDE AZEOTROPE TO ACCELERATE REACTION;
5.75:1 MOLAR RATIO OF PHENOL TO 9-FLUORENONE

To a reactor (reactor design 5) was charged, 75.0 g (0.80 mole) of
5 phenol, 24.98 g (0.1386 mole) of 9-fluorenone and 15.0 g of methylene
chloride. The mixture was heated to 40°C. Catalyst (3-
mercaptopropanesulfonic acid, 0.757 g, 0.0049 mole) was charged to the
reactor and the mixture was stirred. The reaction was followed by HPLC
(analytical method 3).

10   At the end of the reaction, methylene chloride was added to produce a
mixture of 30:30:about 30 percent by weight of methylene
chloride:BHPF:phenol and the mixture was heated to dissolve the
crystalline material. Additional methylene chloride was added to the
solution and the solution was cooled to promote crystallization.

15   The progress of the reaction was shown in Table XIII.

At the end of the reaction, half of the resulting mixture was filtered
and the filter cake was washed with 64 g of methylene chloride. The first
crop of BHPF weighs 7.0 g (dried overnight at 40°C) and was white with very
little pink coloration. A second crop of crystals was collected and
20 washed with 28 g of methylene chloride. Weight, 4.1 g (dried overnight
at 40°C, slightly pink), 99 percent purity after a further washing with
water.

The remainder of the reaction mixture was filtered and the filter cake
was washed with methylene chloride and hot water and dried overnight at 40°
25 C. The recovery was 14 g (51 percent overall recovery), 99 percent purity
by HPLC.

TABLE XIII

Time h:min	Temp. °C	mm. Hg	Observations, Actions
0:0	45	760	Add MPSA, turns dark
0:09	45	760	Add 20 g of methylene chloride; color was dark brownish
0:30	45	760	Lighter brown; reduce pressure to about 180 mm
1:00	45	~180	Seed crystal added; no crystallization observed
2:00	45	~180	Seed crystal added; no crystallization observed
3:00	45	~180	Sample taken; seed crystal added; crystal not dissolving
3:45	45->	~180	Heater set at 40°C; crystals forming
4:00	40	~180	More crystals forming
6:30	40		Sample taken; solid crystalline mass; stirring ineffective; yellowish color; vacuum turned off
19:00	40	760	Sample taken; about 50 to 70% of BHPF crystallized; 33% by weight of methylene chloride added; temperature increased to 58°C
about 20:30	58	760	Temperature lowered to <40°C; methylene chloride added to 80% make up by weight of mixture
	24	760	Cooled to room temperature

C.   REACTION USING METHYLENE CHLORIDE AS SOLVENT: 3.5:1 MOLAR RATIO
OF PHENOL TO FLUORENONE

Phenol (30.0 g, 0.32 mole), 9-fluorenone (16.41 g, 0.0911 mole) and
15.0 g of methylene chloride were charged to a reactor (reactor design 4).
5   The mixture was stirred and heated at 40°C and 1.122 g (0.0072 mole) of
MPSA was added over about 1 minute. Heating was continued at 41°C for the
duration of the reaction. The following observations were made during the
run:

Time (h)	Temp. (°C)	Observations, Actions
0	41	MPSA added; turns orange to brown to dark brown within 30 sec
0.18	41	purple color
0.5	41	sample taken
1.5	41	sample taken
1.67	41	orange mixture seeded with crystals
3	41	sample taken; heater off; left overnight
4	41	heater off
6	room	sample taken; about 80% conversion; more 2:3 adduct than 2,4 adduct

The crystalline solid was removed by filtration and the filter cake was
washed with methylene chloride. A second crop of crystals was recovered
from the mother liquors. The yield was 0.86 g (first crop), 8.66 g
(second crop), 3.5 g (third crop), overall 13 g (41 percent), >99 percent
purity by HPLC (method 3).

25   C.   PHENOL:FLUORENONE MOLAR RATIO OF 15:1; MPSA CATALYST; PHENOL
REMOVED BY DISTILLATION; CRYSTALLIZED FROM METHYLENE CHLORIDE

To a mixture of phenol and fluorenone (15:1 molar ratio), heated to 65°
C, was added 0.0498 equivalent of
3-mercaptopropanesulfonic acid (with respect to fluorenone). The
30   resulting mixture was heated at 65°C for 2 hours, after which the reaction
mixture was washed with water (14 times the volume of the mixture) to
remove MPSA. The washed reaction mixture was distilled to a phenol:BHPF
weight ratio of 1:1 and cooled to bring about crystallization of BHPF.
Crystalline material was removed by filtration, washed with methylene
35   chloride, washed with water and dried to give BHPF (99.8 percent by weight
of 4,4-isomer).

EXAMPLE 26

CONDENSATION OF PHENOL AND ACETONE TO PRODUCE 2,2-BIS-(4-
HYDROXYPHENYL)PROPANE

    A.   FEED CONTAINING 6 percent BY WEIGHT OF ACETONE, PLUS WATER,
5   SOLUBLE CATALYST; BATCH REACTION

    The reaction was carried out in a 2-L jacketed baffled resin pot,
equipped with a condenser and nitrogen purge. Isothermal temperature
control was provided by a fluid material, circulated through the reactor
jacket. Stirring was provided by a Lightnin Labmaster® TS2510 stirrer,
10   equipped with an A-310 impeller.

    To the reactor was charged 1200 g of feed, containing 90.0 percent by
weight of phenol, 6.0 percent by weight of acetone, 1.8 percent by weight
of water and 2.2 percent by weight of MPSA. The mixture was heated at 35°
C. At the end of 2 hours heating, crystallization occurs in the reaction
15   mixture. The reaction was continued 1 hour more, at the end of which 80
percent of the acetone was reacted (HPLC). The reaction mixture was
removed from the reactor and filtered. The weight of recovered crystals
was 17 percent, consisting of a 1:1 adduct of BPA:phenol (molar ratio).
The crystalline adduct was washed with phenol. The washed adduct
20   contained 57.7 percent by weight of 4,4-bisphenol, 160 ppm of 2,4-
bisphenol, 200 ppm of trisphenol, 2270 ppm of other trace bisphenolic
impurities and 1170 ppm of MPSA, the balance being phenol. The mother
liquor contained 8.44 percent by weight of 4,4-bisphenol, 0.26 percent by
weight of 2,4-bisphenol, 0.13 percent by weight of trisphenol 0.62 percent
25   by weight of other bisphenolic impurities, 0.81 percent by weight of
acetone, 2.95 percent by weight of water and 2.78 percent by weight of
MPSA, the balance being phenol.

    B.   REACTION USING RECYCLED MOTHER LIQUORS

    The mother liquor from (A) was charged to a rotary evaporator with
30   make-up phenol (181 g). The evaporator was heated at 50°C for 30 minutes,
at the end of which the conversion of acetone was 90 percent. Pressure
was reduced to 10 mm Hg absolute for 30 minutes, at the end of which the
mixture contained 1.4 percent by weight of water. The acetone content was
below the detection limit.

35   The dried mother liquor was returned to the reactor, along with make-up
phenol, acetone, water and MPSA to give a mixture containing 92.0 percent
by weight of phenol, 4.0 percent by weight of acetone, 1.8 percent by

weight of water and 2.2 percent by weight of MPSA. The total mass
corresponds to (A) minus the weight of samples removed. The mixture was
stirred and heated at 35°C for 3 hours. Crystallization of BPA was
observed after the initial 30 minutes of heating. At the end of 3 hours

5   heating, acetone conversion was 80 percent. The reaction mixture was
processed as in (A). Recycling of the mother liquors was repeated for 12
cycles. Results are given in Tables XIV and XV.

These experiments demonstrate that catalyst and unreacted materials can
be recovered and recycled without adversely affecting the process and that

10   results for successive runs were generally consistent and predictable.

C.   REACTION USING 10 percent BY WEIGHT OF ACETONE IN THE FEED WITH 3
percent BY WEIGHT OF WATER

An experiment was done as in (A), using 1200 g of feed, containing 85.5
percent by weight of phenol, 10.0 percent by weight of acetone, 3.0

15   percent by weight of water and 2.2 percent by weight of MPSA. The
reaction was done at 25°C. Crystalline BPA was visible after 13 hours at
this temperature. At the end of 24 hours, the conversion of acetone was
40 percent.

Crystalline product, removed from the reaction mixture by filtration,

20   constitutes 15 percent of the mixture. The crystals, a 1:1 adduct of
BPA:phenol, were washed with phenol. The washed crystals contain 51.8
percent by weight of the 4,4-isomer, 60 ppm of 2,4-isomer, <20 ppm of
trisphenol, 690 ppm of other trace bisphenols and 840 ppm of MPSA, the
remainder being phenol. The mother liquors contained 6.73 percent by

25   weight of 4,4-isomer, 0.15 percent by weight of 2,4-isomer, 0.08 percent
by weight of trisphenol, 0.76 percent by weight of other bisphenols, 5.71
percent by weight of acetone, 4.97 percent by weight of water and 2.66
percent by weight of MPSA, the remainder being phenol.

TABLE XIV

COMPOSITION F WASHED BISPHENOL A CRYSTALS

Cycle No.	Crystal %	4,4- isomer wt. %	2,4- isomer ppm	Tris- phenol ppm	Other bis- phenol ppm	MPSA ppm
1	17	57.7	160	200	2270	1170
2	22	60.4	420	n/d*	1730	1940
3	17	59.7	460	270	2380	670
4	18	60.7	560	260	2270	1440
5	26	57.9	870	410	1840	1070
6	18	59.3	790	330	2050	2110
7	18	59.3	790	390	2150	740
8	19	59.6	770	280	2100	750
9	22	59.4	840	390	2000	860
10	31	62.5	920	380	2210	1060
11	21	64.0	710	350	2020	1410
12	23	63.0	770	280	1900	1500
Avg. Cycles 7-12	22±5	61±2	800±70	350±50	2100 ±100	1100 ±300

* n/d = not detected

<u>TABLE XV</u>

MOTHER LIQUOR COMPOSITIONS

Cycle No.	4,4-Isomer wt %	2,4-Isomer wt %	Tris-phenol wt %	Other bisphen-olics wt %	Acetone wt %	Water wt %	MPSA wt %
1	8.44	0.26	0.13	0.62	0.81	2.95	2.78
2	7.53	0.48	0.23	0.47	0.63	2.94	2.89
3	8.30	0.55	0.24	0.38	0.79	2.94	2.75
4	8.42	0.66	0.29	0.41	0.70	2.63	2.87
5	8.92	0.78	0.43	0.42	0.86	2.81	2.73
6	8.22	0.86	0.44	0.46	0.73	3.06	2.84
7	7.92	0.87	0.42	0.46	0.66	3.09	2.83
8	8.03	0.91	0.44	0.49	0.58	3.07	2.84
9	8.09	0.84	0.36	0.45	0.72	3.02	2.44
10	6.86	1.03	0.51	0.46	0.25	2.64	2.92
11	7.59	0.78	0.33	0.44	0.51	3.01	2.69
12	7.87	0.84	0.39	0.42	0.27	3.17	3.14
Avg. Cycles 7-12	7.7±0.5	0.88 ±0.09	0.41 ±0.06	0.45 ±0.02	0.5±0.2	3.0±0.2	2.8 ±0.2

<u>Example 27</u>

Preparation of a Representative [(Mercaptoalkyl)(Sulfo)Phenylalkyl]
Sulfonated Polystyrene Catalyst (Designated DPMSA-MER3C)

A. Alkylation

A 15.00 g sample of 200 to 400 mesh chloromethylated polystyrene/2
percent divinylbenzene copolymer beaded (approximately 4.3 mmol Cl/g
resin, approximately 64.5 mmole Cl) known in the art as a Merrifield®
resin (available from Fluka Chemie AG) was added to a round bottom glass
flask (reactor) under a pad of plant nitrogen with a sodium hydroxide
scrubber attached (to trap evolved HCl). (3-Bromopropyl)benzene (102.7 g,
78.4 mL, 8.0 equivalents) was added to the dry resin beads. Dried (over 3
Angstrom molecular sieves) nitrobenzene (50 mL) was added, and the beads
were slowly stirred at room temperature to allow for swelling of the
beads. The reactor was cooled to 0°C in an ice water bath. A 20 mL
sample of 1.0 M aluminum chloride in nitrobenzene available from Aldrich
Chemical Co. was slowly added via syringe to the cold polymer slurry with
rapid stirring over approximately 10 minutes. The mixture turns dark red
as soon as the aluminum chloride solution was added and exotherms to
approximately 4°C within the first 15 minutes of reaction with HCl being

evolved from the solution. After the addition of the AlCl₃/nitrobenzene
solution was complete, the mixture was slowly stirred at 0°C for 2 to 3
hours, then was removed to room temperature and slowly stirred overnight.
The mixture was slowly poured onto ice to quench the aluminum chloride.

5   Then the beads were separated using a glass-fritted funnel with vacuum
filtration. The beads were sequentially washed with water, acetone,
dichloromethane, methanol, dilute aqueous hydrochloric acid, water and
methanol, then were dried overnight in a vacuum oven at 70°C (dry mass
23.52 g).

10   B. Sulfonation

The polymer beads from Example 27A (23.30 g, estimated 161.3 mmole
of phenyl groups) were added to a glass reactor with addition funnel and
NaOH scrubber attached. Dichloromethane (100 mL) was added to the flask
and the beads were allowed to swell (rapid swelling was observed). The

15 slurry was cooled to 0°C in an ice water bath. Chlorosulfonic acid (37.6
g, 21.4 mL, 320 mmole, approximately 2.0 equivalents per equivalent phenyl
groups) was slowly added dropwise over approximately 2 hours to the
polymer slurry at 0°C. The mixture was allowed to slowly warm to room
temperature overnight in the water bath. The mixture was slowly poured

20 onto ice to quench the excess chlorosulfonic acid, then the beads were
separated using a glass-fritted funnel with vacuum filtration. The beads
were then washed extensively with water. Water was added to make a
slurry, then solid sodium bicarbonate was slowly added in small portions
over approximately 2 hours until no more bubbling was observed (all active

25 acid sites neutralized). The mixture was allowed to stand 3 days in the
aqueous sodium bicarbonate solution (some additional bead swelling was
observed over this time period). The beads were washed with water and
transferred to a glass reactor with 100 mL of water. The beads were then
heated to 70-80°C over 2 hours to ensure hydrolysis of any residual

30 sulfonyl chloride groups.

          C. Thiolation

The aqueous polymer slurry from Example 27B was cooled to room
temperature. Sodium bicarbonate was slowly added until the slurry was
neutral (no bubbling observed), then additional sodium bicarbonate (27.1

35 g, 323 mmol) was added to the aqueous bead slurry. Thiolacetic acid (24.6
g, 23.1 mL, 323 mmol) was added to an addition funnel. The reactor was
evacuated and refilled with nitrogen several times to minimize the air

content. The thiolacetic acid was slowly added over approximately 15 to
20 minutes to the aqueous bead slurry with rapid stirring. The addition
rate was adjusted to control the effervescent evolution of carbon dioxide
which was formed in the neutralization process. After the thiolacetic

5   acid addition was complete, the mixture was heated to 70°C and was allowed
to react overnight with minimal stirring. The mixture was then cooled to
room temperature and the beads were collected by filtration using a
fritted-glass funnel. The beads were washed extensively with water, then
with dichloromethane, and then washed again with water. The beads were

10   transferred back to the glass reactor, then concentrated (12 molar)
hydrochloric acid (100 mL) was added. The mixture was heated with mild
stirring to 50°C for 4 to 5 hours, then was cooled to room temperature.
Deionized water (100 mL) was added and the beads were again collected by
filtration using a fritted-glass funnel. The beads were washed with

15   water, then were washed extensively (approximately 500 mL) with dilute
(approximately 3 molar) aqueous hydrochloric acid. The beads were then
washed again with deionized water and finally were washed with methanol to
displace the water and shrink the polymer beads. The beads were dried
overnight in a vacuum oven at 70 °C (dry mass 34.17 g). The final polymer

20   catalyst was designated as DPMSA-MER3C

D.   Preparation of Three-Carbon DPMSA Polymer From Merrifield®
Resin Beads

Another mercaptosulfonic acid polymer was prepared using the
procedure of steps A to C of Example 27, except using a chloromethylated

25   polystyrene resin (2 percent divinylbenzene, 200 to 400 mesh,
approximately 4.3 mmol Cl/g resin), a Merrifield® resin commercially
available from Fluka Chemie AG as the polymeric support and (3-
bromopropyl)benzene in the alkylation step of the reaction. The resulting
polymer was identified as DPMSA-MER3C.

30   E.   Preparation of Three-Carbon DPMSA Polymer From Chloromethylated
Gel-Resin Beads

Another mercaptosulfonic acid polymer was prepared using the
procedure of steps A to C of Example 27, except using a chloromethylated
1.5 percent crosslinked polystyrene gel-resin (-30+70 mesh, approximately

35   4.3 mmol Cl/g resin) as the polymeric support and (3-bromopropyl) benzene
in the alkylation step of the reaction. This polymer was identified as
DPMSA-1.5X3C.

F.   Preparation of Two-Carbon DPMSA Polymer From Chloromethylated
Gel-Resin Beads

Another mercaptosulfonic acid polymer was prepared using the
procedure of steps A to C of Example 27, except using a chloromethylated
5   1.5 percent crosslinked polystyrene gel-resin (-30+70 mesh, approximately
4.3 mmol Cl/g resin) as the polymeric support and (2-bromoethyl) benzene
in the alkylation step of the reaction. This polymer was identified as
DPMSA-1.5X2C.

G.   Preparation of three Carbon DPMSA from 6 percent Crosslinked
10 Macroporous Resin

Another mercaptosulfonic acid polymer was using the procedure of
steps A to C of Example 27, except using a chloromethylated 6 percent
crosslinked macroporous polystyrene resin (approximately 30 to 70 mesh,
approximately 4.3 mmol Cl/g resin) as the polymeric support and (3-
15 bromopropyl)benzene in the alkylation step of the reaction. This polymer
was identified as DPMSA-6/42-3C.

H.   Preparation of three Carbon DPMSA from 6.5 percent Crosslinked
Gel Resin

Another mercaptosulfonic acid polymer was using the procedure of
20 steps A to C of Example 27, except using a chloromethylated 6.5 percent
crosslinked uniform particle size polystyrene gel-resin (380 micron,
approximately 4.3 mmol Cl/g resin) as the polymeric support and
(3-bromopropyl)benzene in the alkylation step of the reaction. This
polymer was identified as DPMSA-6.5X3C.

25 EXAMPLE 28

EVALUATION OF CATALYSTS IN CONTINUOUS PROCESSES

A fixed bed downflow reactor, having a volume of 10-mL, was constructed
from a vertical tube, filled with catalyst. External to the catalyst bed
was a preheater area, packed with glass wool. Ancillary equipment
30 includes a pressure regulator, relief valve, pump and heater for the feed.
The feed was heated by heating fluid, circulated through the feed pot, and
was kept under a nitrogen pad.

The feed was phenol (99.9 percent) and fluorenone (about 99 percent) in
a 21:1 molar ratio.

35 The heating fluid, heating tape and reactor were turned on. The
selected catalyst was slurried in phenol at about 45°C. Catalyst-phenol
mixture was pigetted into the reactor, at the bottom of which a plug of

glass wool/glass beads was placed to prevent catalyst from leaving the reactor. The phenol:fluorenone was added to the feed pot at 55°C. The pressure was adjusted to about 0.34 bars.

5   Phenol:fluorenone feed was introduced into the reactor and the composition of the effluent from the reactor was followed by HPLC.

The following results were obtained:

Table XVI

PMBSA-Mer catalyst (Example 9C) at 50°C:

productivity　　　1.4 g BHPF/g cat h

conversion　　　time (h)　　% fluorenone conversion

time (h)	% fluorenone conversion
0.33	99.7
28	100.0
53	100.0
69	99.7
89	99.9
113	100.0
137	99.8
144	99.6
162	99.6

selectivity 98% 4,4-BHPF

PMBSA-XEBr (Example 9D) at 69°C:

productivity　　　0.6 g BHPF/g cat h

conversion　time (h)　　% fluorenone conversion

time (h)	% fluorenone conversion
2	99.8
15	100.0
39	100.0
63	98.9
79	99.0
103	95.5
127	87.1
164	83.4

selectivity 98% 4,4-BHPF

PMBSA-XEC1 (Example 9E) at 56°C:

      productivity   1.48 g BHPF/g cat h

      conversion time (h)   % fluorenone conversion

time (h)	% fluorenone conversion
2	99.2
27	99.1
63	99.3
87	98.7
111	98.9
135	98.6
159	98.3
164	98.0

    selectivity 98% 4,4-BHPF

XEMSA-11C (Example 22D) at 60°C:

    conversion time (h) % fluorenone conversion

time (h)	% fluorenone conversion
1	99.2
17	94.4
41	92.2
65	91.0

DPMSA-MER3C (Example 27D) at 50°C:

      selectivity 98% p,p-BHPF

      productivity 4 lb BHPF/ lb catalyst/hour = 4 kg/kg/h

      conversion time (h)   % fluorenone conversion

time (h)	% fluorenone conversion
20	99.9
24	99.9
39	99.9
48	100.0
66.5	100.0
75.5	98.9
99.5	99.1
103	98.6
104	98.7

XEMSA-5C (Example 22) at 55°C:

      selectivity 98% p,p-BHPF

      productivity 0.43 LB BHPF/LB catalyst/hour =0.43 kg/kg/h

conversion time (h)	percent fluorenone conversion
4	99.7
22	100.0
46	100.0
70	100.0
77	99.7
94	99.7
118	99.7
142	99.5
144	99.4
168	99.3
192	99.0
216	99.0
240	98.6
264	98.6

DPMSA-XE3C (Example 27A-C) at 56°C:

      selectivity 98 percent 4,4-BHPF

conversion time (h)	% fluorenone conversion
30	98.0
48	95.1
72	94.7
96	92.3
123	87.3
144	86.1
170	83.8
240	77.1

These results show that PMBSA, XEMSA, and DPMSA catalysts of the invention can exhibit stability over time, thus, have very useful lifetimes.

EXAMPLE 29

CONTINUOUS PROCESS FOR MAKING BHPF USING MERCAPTOPROPANESULFONIC ACID
CATALYST

The reactor comprises a three-staged continuous reactor (isothermal

5 perfectly stirred type). The reaction was run at 46°C at a 21:1 molar

ratio of phenol:fluorenone (98 percent, Aldrich), the amount of MPSA being

0.05 to 0.07 equivalent of MPSA:mole of fluorenone. The composition of

the products was followed by HPLC.

The reaction was continued for 228 hours, at the end of which

10 fluorenone conversion was 99.95 percent (reactor 2) or 99.9 percent

(reactor 1) and selectivity to 4,4-BHPF was 98.32 percent (reactor 2) or

95.2 percent (reactor 1).

EXAMPLE 30

EVALUATION OF CATALYST OF EXAMPLE 22D (XEMSA-5C) IN CONTINUOUS PROCESS FOR

15 MAKING BISPHENOL A

The reactor comprises a vertical upflow column of stainless steel

tubing, packed with resin atop a screen and glass beads. The column was

heated by a water jacket. The progress of the reaction was followed as

above by HPLC.

20 The following results were obtained:

Table XVII

Test		25% promoted *DOWEX™ 50Wx4	XEMSA-5C Example 22D
Acid capacity			
dry	meq/g	4.0	3.5
wet	meq/mL	0.84	1.17
Swell test			
phenol/water vol.		0.55	0.72
Reaction tests			
30 min res. time			
4% acetone, 65°C			
4,4	% by wt	12.7	14.0
conversion		0.83	>0.95
productivity		8.2	9.0 ± 0.2
2,4/4,4		0.28	0.024 ± 0.001
6% acetone, 65°C			
4,4	% by wt	~15	19.1 ± 0.6
conversion		~0.7	0.92
productivity		~10	12.2 ± 0.4
2,4/4,4		~0.27	0.025 ± 0.003
4% acetone, 55°C			
4,4		10.7	13.0 ±0.1
conversion		0.67	0.92 ± 0.01
productivity		7.2	8.3 ± 0.06
2,4/4,4		0.21	0.019 ± 0.001

*Trademark of The Dow Chemical Company

EXAMPLE 31

PREPARATION OF BISPHENOL F

5   Phenol and formaldehyde were reacted to produce bisphenol F. Similar
results were obtained.

     The preceding examples can be repeated with similar success by
substituting the generically or specifically described reactants and/or
operating conditions of this invention for those used in the preceding
10   examples.

From the foregoing description, one skilled in the art can easily
ascertain the essential characteristics of this invention and without
departing from the spirit and scope thereof, can make various changes and
modifications of the invention to adapt it to various usages and
5   conditions.

Example 32

    Alternate Preparation of a Representative [(Mercaptoalkyl)(Sulfo)-
Phenylalkyl] Sulfonated Polystyrene Catalyst (Designated DPMSAA-0.25-
1.5X2C)

10   A Preparation of (2-Bromoethyl)benzyl Chloride

(A1) In an extension of the procedure described by Selva, M; Trotta, F.;
and Tundo, P. Synthesis, 1991, 1003-1004, (2-bromoethyl)benzylchloride was
prepared by the following procedure:

    Concentrated sulfuric acid (132 mL) was slowly added to ice cold
15   deionized water (66 mL) in a 1 L three-necked glass reactor fitted with a
mechanical stirrer, reflux condenser, and temperature probe. The reactor
containing the sulfuric acid solution was cooled in an ice bath, then (2-
bromoethyl)benzene (92.5 g, 0.50 mol) was added followed by 50 percent
tetrabutylammonium chloride in water (10 g of solution), paraformaldehyde
20   (20.0g, 0.666 mol, 1.33 equivalents), and finally sodium chloride (80.0 g,
1.37 mol, 2.74 equivalents). The slurry was stirred at approximately 1000
rpm (very vigorous) and heated to 80°C for 2.25 hours. The reaction was
less than 50 percent complete as determined by gas chromatographic
analysis. Additional paraformaldehyde (20.0 g, 0.666 mol, 1.33
25   equivalents) was added and the mixture was stirred (600-700 rpm) an
additional 3.5 hours at 80°C. The reaction was approximately 50 percent
complete as determined by gas chromatographic analysis. The mixture was
allowed to cool and was transferred to a separatory funnel. The organic
phase was separated and saved for further reaction.

30   (A2) Alternatively, (2-Bromoethyl)benzene (92.5 g, 0.50 mol),
concentrated (12 molar) hydrochloric acid (125 mL, 1.5 mole HCl, 3
equivalents HCl), and paraformaldehyde (22.5 g, 0.75 mol, 1.5 equivalents)
were added to a 1 L three-necked glass reactor fitted with a mechanical
stirrer, addition funnel, and temperature probe. Concentrated sulfuric
35   acid (111 mL, approximately 205 g, approximately 4 equivalents of sulfuric
acid) was added to the addition funnel. A small portion (approximately
10-15 mL) of the sulfuric acid was added to the reaction mixture from the

addition funnel and the slurry was heated to 80°C with stirring at
approximately 1000 rpm. After the reaction reaches 80°C, the remaining
concentrated sulfuric acid was added dropwise over 3 hours. After an
addition 1 hour reaction time, the reaction was less than 50 percent
5   complete as determined by gas chromatographic analysis. The mixture was
allowed to cool and was transferred to a separatory funnel. The organic
phase was separated and saved for further reaction.

The combined products from Example 32, parts A1 and A2 containing
unreacted (2-bromoethyl)benzene and chloromethylated (2-bromoethyl)benzene
10   products (mixture of isomers) were further chloromethylated according to
the procedure described in part A1. The reaction was performed using
sufficient time and reagent (paraformaldehyde, sodium chloride, sulfuric
acid) charges to completely consume the (2-bromoethyl)benzene starting
material, giving a mixture of (2-bromoethyl)benzyl chloride isomers along
15   with higher-boiling by-products. The mixture of (2-bromoethyl)benzyl
chloride isomers was isolated by oil-pump vacuum bulb-to-bulb Kugelrohr
distillation (up to 140-145°C). The isolated product was a water-white
oil which solidifies upon standing at room temperature. Gas
chromatography analysis shows that unreacted (2-bromoethyl)benzene and the
20   higher boiling by-products were essentially absent from the distilled (2-
bromoethyl)benzyl chloride isomers product.

B. Alkylation

Styrene/divinylbenzene co-polymer resin beads (10.00 g, -30+70 mesh,
1.5 percent divinylbenzene, approximately 96.0 mmole styrene repeat units)
25   were added to a round bottom glass flask (reactor) under a pad of nitrogen
with a sodium hydroxide scrubber attached (to trap evolved HCl). A
solution of (2-bromoethyl)benzyl chloride (mixture of aromatic ring
isomers, predominately para) (10.0 g, 0.238 equivalents based upon styrene
repeating units) in
30   1,2-dichloroethane (25 mL) was added to the dry resin beads. The beads
were allowed to swell for approximately 5 to 10 minutes, then additional
1,2-dichloroethane (35 mL) was added to the swollen beads. Anhydrous
tin(IV) chloride (2.5 mL, approximately 5.57 g, approximately 21.4 mmol)
was slowly added via syringe to the polymer slurry at room temperature
35   over approximately 10 minutes with rapid stirring. The mixture turned
light yellow when the tin(IV) chloride was added. The mixture was slowly
warmed (in 5°C increments) to 40°C over approximately 30 minutes and was

allowed to react at 40°C for 1 hour. At this time the light orange
mixture was slowly warmed (in 5°C increments) to 60°C over approximately 1
hour 30 minutes and was allowed to react overnight at 60°C with slow
stirring. After overnight reaction, the mixture was cooled to room
5   temperature and was quenched by slowly adding methanol to the well-stirred
polymer slurry. The beads were separated from the solution using a glass-
fritted funnel with vacuum filtration. The beads were sequentially washed
(three portions each) with dichloromethane, water, tetrahydrofuran, and
methanol, then the beads were dried overnight in a vacuum oven at 80°C
10   (dry mass 13.89 g). Theoretical mass yield = 14.49 g. Alkylation yield
(by mass uptake) = 87 percent. Approximate degree of polymer
functionalization (by mass yield) = 0.21.

        C. Sulfonation

        The polymer beads from Example 32B (13.89 g, estimated 116 mmole of
15   phenyl groups) were added to a glass reactor with addition funnel and NaOH
scrubber attached. Dichloromethane (75 mL) was added to the flask and the
beads were allowed to swell (rapid swelling was observed). The slurry was
cooled to approximately 3 to 5 °C in an ice water bath. Chlorosulfonic
acid (11.7 mL, approximately 20.5 g, approximately 176 mmol, approximately
20   1.5 equivalents per equivalent of phenyl groups) was slowly added dropwise
over approximately 30 minutes to the cold polymer slurry with stirring.
The mixture was allowed to react at approximately 3 to 5°C in an ice water
bath for 1 hour. The mixture was removed from the ice bath and allowed to
warm to room temperature over 2 hours 45 minutes. At this time, the
25   polymer slurry was again cooled to 3-5°C in an ice water bath, and water
was slowly added with rapid stirring to quench the excess chlorosulfonic
acid. The beads were separated using a glass-fritted funnel with vacuum
filtration. The beads were then washed extensively with water. Water was
added to make a slurry, then solid sodium bicarbonate was slowly added in
30   small portions with stirring until no more bubbling was observed (all
active acid sites were neutralized). The beads were washed with water and
transferred back to the glass reactor with 100 mL of water. The beads
were then heated to 60 to 70°C over 2 hours to ensure hydrolysis of any
residual sulfonyl chloride groups.

35   D. Thiolation

        The aqueous polymer slurry from Example 32C (estimated approximately
20 mmole Br) was cooled to room temperature. Sodium bicarbonate was

slowly added until the slurry was neutral (no bubbling observed), then additional sodium bicarbonate (5.30 g, 63.0 mmol, approximately 3 equivalents relative to estimated bromine content in beads) was added to the aqueous bead slurry. Thiolacetic acid (4.5 mL, approximately 4.8 g,

5 approximately 63 mmol, approximately 3 equivalents relative to estimated bromine content in beads) was added to an addition funnel. The reactor was evacuated and refilled with nitrogen several times to minimize the air content. The thiolacetic acid was slowly added over approximately 10-15 minutes to the aqueous bead slurry at room temperature with rapid

10 stirring. The thiolacetic acid addition rate was adjusted to control the effervescent evolution of carbon dioxide which was formed in the neutralization process. After the thiolacetic acid addition was complete, the mixture was heated to 70°C and was allowed to react overnight with minimal stirring. The mixture was then cooled to room temperature and the

15 beads were collected by filtration using a fritted-glass funnel. The beads were washed extensively with water, then with dichloromethane (optional), and then washed again with water. The beads were transferred back to the glass reactor, then concentrated (12 molar) hydrochloric acid (100 mL) was added. The mixture was heated with mild stirring to 50°C for

20 2-3 hours, then was cooled to room temperature. Deionized water (100 mL) was added and the beads were again collected by filtration using a fritted-glass funnel. The beads were washed with water, then were washed extensively (approximately 500 mL) with dilute (approximately 3 molar) aqueous hydrochloric acid. The beads were then washed again with

25 deionized water and were transferred to a storage bottle without any additional drying. The final polymer catalyst has a titrated water-wet (water swollen) acid capacity of 0.80 milliequivalent/mL catalyst. The final polymer catalyst was designated as DPMSAA-0.25-1.5X2C

E. Preparation of DPMSAA Resin with 0.71 Equivalents Alkylation

30 Another mercaptosulfonic acid polymer was prepared from 1.5 percent crosslinked styrene/divinylbenzene co-polymer beads (-30+70 mesh) using the procedure described in steps B-D of Example 32, except using 0.71 equivalents of (2-bromoethyl)benzyl chloride in the alkylation reaction. Chlorosulfonic acid (2.0 equivalents relative to the calculated total

35 equivalents of phenyl groups in the polymer) was used in the sulfonation reaction. Thiolacetic acid and sodium bicarbonate (3.0 equivalents of each reagent relative to the calculated amount of bromine in the polymer)

were used in the thiolation reaction. The mass yield of polymer obtained
from the alkylation reaction corresponds to a 83 percent yield in the
alkylation reaction and a degree of functionality of 0.59. The final
polymer catalyst has a titrated water-wet (water swollen) acid capacity of
5   0.94 milliequivalent/mL catalyst. The final polymer catalyst was
designated as DPMSAA-0.75-1.5X2C.

     F.   Preparation of DPMSAA Resin with 0.43 Equivalents Alkylation

Another mercaptosulfonic acid polymer was prepared from 1.5 percent
crosslinked styrene/divinylbenzene co-polymer beads (-30+70 mesh) using
10   the procedure described in steps B-D of Example 32, except using 0.43
equivalents of (2-bromoethyl)benzyl chloride in the alkylation reaction.
Chlorosulfonic acid (2.0 equivalents relative to the calculated total
equivalents of phenyl groups in the polymer) was in the sulfonation
reaction. Thiolacetic acid and sodium bicarbonate (3.0 equivalents of
15   each reagent relative to the calculated amount of bromine in the polymer)
were used in the thiolation reaction. The mass yield of polymer obtained
from the alkylation reaction corresponded to a 81 percent yield in the
alkylation reaction and a degree of functionality of 0.35. The final
polymer catalyst has a titrated water-wet (water swollen) acid capacity of
20   0.85 milliequivalent/mL catalyst. The final polymer catalyst was
designated as DPMSAA-0.45-1.5X2C.

     G.   Preparation of DPMSAA with 0.095 Equivalents Alkylation

Another mercaptosulfonic acid polymer was prepared from 1.5 percent
crosslinked styrene/divinylbenzene co-polymer beads (-30+70 mesh) using
25   the procedure described in steps B-D of Example 32, except using 0.095
equivalents of (2-bromoethyl)benzyl chloride in the alkylation reaction.
Chlorosulfonic acid (1.5 equivalents relative to the calculated total
equivalents of phenyl groups in the polymer) was used in the sulfonation
reaction. Thiolacetic acid and sodium bicarbonate (3.0 equivalents of
30   each reagent relative to the calculated amount of bromine in the polymer)
were used in the thiolation reaction. The mass yield of polymer obtained
from the alkylation reaction corresponds to a 99 percent yield in the
alkylation reaction and a degree of functionality of 0.094. The final
polymer catalyst has a titrated water-wet (water swollen) acid capacity of
35   0.80 milliequivalent/mL catalyst. The final polymer catalyst was
designated as DPMSAA-0.10-1.5X2C.

H.   Preparation of DPMSAA with 0.42 Equivalents of (2-
Bromoethyl)benzylchloride Alkylation and 0.30 Equivalents of Benzyl
Chloride Alkylation

     Another mercaptosulfonic acid polymer was prepared from 1.5 percent

5 crosslinked styrene/divinylbenzene co-polymer beads (-30+70 mesh) using
the procedure described in steps B-D of Example 32, except using 0.42
equivalents of (2-bromoethyl)benzyl chloride and 0.30 equivalents of
benzyl chloride in the alkylation reaction. Chlorosulfonic acid (2.0
equivalents relative to the calculated total equivalents of phenyl groups

10 in the polymer) was used in the sulfonation reaction. Thiolacetic acid
and sodium bicarbonate (3.0 equivalents of each reagent relative to the
calculated amount of bromine in the polymer) were used in the thiolation
reaction. The final polymer catalyst has a titrated water-wet (water
swollen) acid capacity of 0.94 milliequivalent/mL catalyst. The final

15 polymer catalyst was designated as DPMSAA-0.45/0.30-1.5X2C.

     I.   Preparation of DPMSAA Resin having 0.423 Equivalents.
Alkylation

     Another mercaptosulfonic acid polymer was prepared from 1.5 percent
crosslinked styrene/divinylbenzene co-polymer beads (-30+70 mesh) using

20 the procedure of steps B-D of Example 32, except using 0.423 equivalents
of (2-bromoethyl)benzyl chloride in the alkylation reaction and directly
carrying the polymer slurry obtained from the alkylation reaction directly
on to the sulfonation reaction without any quenching, isolation, or
washing steps after the alkylation reaction. Chlorosulfonic acid (1.25

25 equivalents relative to the total equivalents of phenyl groups present in
all reactants) was added directly to the polymer slurry after the
alkylation reaction was complete. Workup and subsequent isolation of the
product after sulfonation was as in Example 32, except that more extensive
washing was required to remove soluble reaction by-products from the

30 polymer slurry. Thiolacetic acid and sodium bicarbonate (3.0 equivalents
of each reagent relative to the estimated maximum amount of bromine
present in the polymer) were used in the thiolation reaction. The final
polymer catalyst has a titrated water-wet (water swollen) acid capacity of
0.78 milliequivalent/mL catalyst. The final polymer catalyst was

35 designated as DPMSAA-0.45NW-1.5X2C.

J.   Preparation of DPMSAA Resin with 0.238 Equivalents Alkylation

Another mercaptosulfonic acid polymer was prepared from 1.5 percent crosslinked styrene/divinylbenzene co-polymer beads (-30+70 mesh) using a variation of the procedure described in Example 32. The alkylation and
5   sulfonation reactions were performed in one step utilizing chlorosulfonic acid as the alkylation catalyst and sulfonation reagent.

Styrene/divinylbenzene co-polymer resin beads (10.00 g, -30+70 mesh, 1.5 percent divinylbenzene, approximately 96.0 mmol styrene repeat units) were added to a round bottom glass flask (reactor) under a pad of plant
10   nitrogen with a sodium hydroxide scrubber attached (to trap evolved HCl). A solution of (2-bromoethyl)benzyl chloride (mixture of aromatic ring isomers, predominately para) (5.32 g, 0.238 equivalents based upon styrene repeat units) in

1,2-dichloroethane (25 mL) was added to the dry resin beads. The beads
15   were allowed to swell for approximately 5 to 10 minutes, then additional 1,2-dichloroethane (35 mL) was added to the swollen beads. The slurry was cooled 2 to 3°C in an ice bath, then chlorosulfonic acid (12.0 mL, approximately 21.0 g, 1.5 equivalents based upon total equivalents of phenyl groups in the mixture) was added slowly dropwise over approximately
20   1 hour 45 minutes. The mixture was allowed to stir an additional 1 hour at 3 to 4°C, then was removed to room temperature and allowed to react an additional 1.5 hours. The mixture was then cooled in an ice water bath and water was slowly added to quench the excess chlorosulfonic acid. Thereafter the beads were isolated according to the procedure described in
25   part C of Example 32. Likewise, the thiolation reaction was as in part D of Example 32 using thiolacetic acid and sodium bicarbonate (3.0 equivalents of each reagent relative to the estimated maximum amount of bromine in the polymer). The final polymer catalyst has a titrated water-wet (water swollen) acid capacity of 0.94 milliequivalent/mL catalyst.
30   The final polymer catalyst was designated as DPMSAA-2S-0.25-1.5X2C.

K.   Preparation of DPMSAA Resin Having 6.5 percent Crosslinking

Another mercaptosulfonic acid polymer was prepared from 6.5 percent crosslinked styrene/divinylbenzene co-polymer beads (380 micron uniform particle size spheres) using the procedure described in steps B to D of
35   Example 32, except using 0.427 equivalents of (2-bromoethyl)benzyl chloride in the alkylation reaction.

Chlorosulfonic acid (1.5 equivalents relative to the calculated total equivalents of phenyl groups in the polymer) was used in the sulfonation reaction. Thiolacetic acid and sodium bicarbonate (3.0 equivalents of each reagent relative to the calculated amount of bromine

5   in the polymer) were used in the thiolation reaction. The mass yield of polymer obtained from the alkylation reaction corresponded to a 57 percent yield in the alkylation reaction and a degree of functionality of 0.24. The final polymer catalyst has a titrated water-wet (water swollen) acid capacity of 1.75 milliequivalent/mL catalyst. The final polymer catalyst

10   was designated as DPMSAA-0.45-6.5X2C.

     L. Preparation of DPMSAA Resin with 0.25 Equivalents Alkylation and Having 1.8 percent Crosslinking

     Another mercaptosulfonic acid polymer was prepared from 1.8 percent crosslinked styrene/divinylbenzene copolymer beads (-25+40 mesh) using the

15   procedure described in steps B through D of Example 32, except using 0.25 equivalents of (2-bromoethyl)benzyl chloride in the alkylation reaction.

     Chlorosulfonic acid (1.5 equivalents relative to the calculated total equivalents of phenyl groups in the polymer) was used in the sulfonation reaction. Thiolacetic acid and sodium bicarbonate (3.0

20   equivalents of each reagent relative to the calculated amount of bromine in the polymer) were used in the thiolation reaction. The mass yield of polymer obtained from the alkylation reaction corresponds to an 86 percent yield in the alkylation reaction and a degree of functionality of 0.22. The final polymer catalyst had a titrated water-wet (water swollen) acid

25   capacity of 0.85 milliequivalent/mL catalyst. The final polymer catalyst was designated as DPMSAA-0.25-1.8X2C.

     M. Preparation of DPMSAA Resin with 0.10 Equivalents Alkylation and Having 1.8 percent Crosslinking

     Another mercaptosulfonic acid polymer was prepared from 1.8 percent

30   crosslinked styrene/divinylbenzene co-polymer beads (-25+40 mesh) using the procedure described in steps B to D of Example 32, except using 0.10 equivalents of (2-bromoethyl)benzyl chloride in the alkylation reaction. Chlorosulfonic acid (1.5 equivalents relative to the calculated total equivalents of phenyl groups in the polymer) was used in the sulfonation

35   reaction. Thiolacetic acid and sodium bicarbonate (3.0 equivalents of each reagent relative to the calculated amount of bromine in the polymer) were used in the thiolation reaction. The final polymer catalyst has a

titrated water-wet (water swollen) acid capacity of 0.81

milliequivalent/mL catalyst. The final polymer catalyst was designated as

DPMSAA-0.10-1.8X2C.

N. Preparation of 1.5 percent Crosslinked DPMSAA Resin with 0.10

5   Equivalents Alkylation and Using Sodium Hydrosulfide in the Thiolation

Reaction

Another mercaptosulfonic acid polymer was prepared from 1.5 percent

crosslinked styrene/divinylbenzene co-polymer beads (-30+70 mesh) using a

variation of the procedure described in steps B to D of Example 32, except

10   using 0.10 equivalents of (2-bromoethyl)benzyl chloride in the alkylation

reaction and sodium hydrosulfide in the thiolation reaction.

Chlorosulfonic acid (1.5 equivalents relative to the calculated total

equivalents of phenyl groups in the polymer) was used in the sulfonation

reaction. Sodium hydrosulfide (6.4 equivalents relative to the calculated

15   amount of bromine in the polymer) was used in the thiolation reaction.

The mass yield of polymer obtained from the alkylation reaction

corresponds to a degree of functionality of 0.10. The final polymer

catalyst has a titrated water-wet (water swollen) acid capacity of 0.82

milliequivalent/mL catalyst. The final polymer catalyst was designated as

20   DPMSAA-AT-0.10-1.5X2C.

O. Preparation of DPMSAA Resin with 0.25 Equivalents Alkylation and

Having 4 percent Crosslinking

Another mercaptosulfonic acid polymer was prepared from 4 percent

crosslinked styrene/divinylbenzene co-polymer beads (360 micron uniform

25   particle size spheres) using the procedure described in steps B-D of

Example 32, except using 0.25 equivalents of (2-bromoethyl)benzyl chloride

in the alkylation reaction. Chlorosulfonic acid (1.5 equivalents

relative to the calculated total equivalents of phenyl groups in the

polymer) was used in the sulfonation reaction. Thiolacetic acid and

30   sodium bicarbonate (3.0 equivalents of each reagent relative to the

calculated amount of bromine in the polymer) were used in the thiolation

reaction. The mass yield of polymer obtained from the alkylation reaction

corresponds to a 73 percent yield in the alkylation reaction and a degree

of functionality of 0.18. The final polymer catalyst was designated as

35   DPMSAA-0.25-4X2C.

P. Preparation of DPMSAA Resin with 0.10 Equivalents Alkylation and

Having 4 percent Crosslinking

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Another mercaptosulfonic acid polymer was prepared from 4 percent crosslinked styrene/divinylbenzene co-polymer beads (360 micron uniform particle size spheres) using the procedure described in steps B-D of Example 32, except using 0.10 equivalents of (2-bromoethyl)benzyl chloride

5   in the alkylation reaction. Chlorosulfonic acid (1.5 equivalents relative to the calculated total equivalents of phenyl groups in the polymer) was used in the sulfonation reaction. Thiolacetic acid and sodium bicarbonate (3.0 equivalents of each reagent relative to the calculated amount of bromine in the polymer) were used in the thiolation reaction. The mass

10 yield of polymer obtained from the alkylation reaction corresponds to an 74 percent yield in the alkylation reaction and a degree of functionality of 0.074. The final polymer catalyst was designated as DPMSAA-0.10-4X2C.

Example 33

Evaluation of Catalysts in a Continuous Process

15 A three-stage up-flow reactor was constructed from three vertical stainless steel tubes with sampling ports between each section. Each reactor stage was water jacketed for temperature control with all connecting lines heat-traced to prevent reactor line plugging. Likewise the 2L reactor feed tank was jacketed so that precise control of the

20 reactor feed can be obtained. From the feed tank, feed flows through an electrically heat-traced section of tubing for control of feed input temperature.

Each reactor section was packed with 10-20 mL of water-wet catalyst.

The reactor feed consists of a solution of 4 weight percent acetone

25 in phenol. The acetone:phenol mixture was precisely metered into the temperature controlled reactor system at a defined combination of flow rate (1.0 mL/min to 2.0 mL/min) and reactor temperature (55°C to 65°C). Upon start-up of each new loading of catalyst, the feed passes through the catalyst for at least 12 hours before measurements were recorded to remove

30 water from the catalyst. Product composition of the reactor effluent from each of the three stages was analyzed by HPLC while gas chromatography was used to analyze for acetone and water. The results obtained from tests of the catalysts at various times of reaction (reactor residence times) were provided in Table XIX. Productivity was expressed in terms of pounds of

35 bisphenol A produced per hour per cubic foot of water-swollen catalyst charged into the reactor. (NOTE: Unless otherwise noted, all of the catalyst results were obtained at 55°C.)

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Table XIX

CATALYST	Res. Time	Acetone Conv.(%)	Prod. lb/hr/ft3	op/pp (%)	tris/pp (%)	Cyclics/pp (%)	tot imp/pp (%)
65 C DOWEX 50Wx4, 25% Prom.	10	61.47%	18.03	2.524%	0.702%	0.535%	5.393%
	20	77.69%	11.53	2.722%	0.648%	0.472%	5.204%
	30	84.52%	8.34	2.826%	0.628%	0.455%	5.149%
55 C DOWEX 50Wx4, 25% Prom.	10	49.28%	13.83	1.983%	0.783%	0.328%	5.297%
	20	66.16%	9.51	2.102%	0.675%	0.292%	4.862%
	30	73.02%	7.06	2.163%	0.692%	0.257%	4.838%
DPMSA-MER3C	5	84.28%	49.76	1.479%	0.549%	0.879%	5.053%
	10	97.63%	29.92	1.456%	0.491%	0.828%	3.829%
	15	100.00%	20.62	1.449%	0.553%	0.836%	3.831%
DPMSA-1.5X3C	7.5	46.34%	18.12	1.884%	0.855%	0.929%	5.803%
	15	71.71%	14.51	1.769%	0.794%	0.890%	4.359%
	22.5	81.41%	11.21	1.733%	0.730%	0.819%	4.951%
DPMSA-1.5X2C	7.5	44.74%	16.13	1.577%	0.958%	1.524%	7.512%
	15	74.84%	14.31	1.537%	0.800%	1.298%	4.840%
	22.5	88.14%	11.53	1.534%	0.790%	1.167%	5.372%
DPMSA-6/42-3C	7.5	11.34%	3.08	2.519%	0.000%	2.096%	12.918%
	15	29.62%	4.38	2.203%	0.383%	2.044%	15.295%
	22.5	52.79%	6.12	1.946%	0.296%	1.999%	12.032%
DPMSA-6.5X3C	7.5	1.68%	0.13	0.000%	3.029%	0.000%	1.290%
	15	1.11%	0.05	0.000%	2.166%	0.000%	2.166%
	22.5	0.34%	0.10	0.524%	0.687%	0.000%	0.671%
DPMSAA-0.75-1.5X2C (0.75 funct.)	7.5	90.84%	34.65	1.583%	0.992%	0.570%	4.298%
	15	98.43%	20.02	1.596%	0.912%	0.513%	3.707%
	22.5	100.00%	13.30	1.521%	0.922%	0.677%	3.478%
DPMSAA-0.75-1.5X2C (2 ML)	3.75	66.83%	51.95	1.571%	0.886%	0.687%	5.074%
	7.5	89.68%	35.41	1.590%	0.975%	0.565%	4.400%
	11.25	94.95%	25.26	1.617%	0.945%	0.528%	4.142%
DPMSAA-0.45-1.5X2C	7.5	88.41%	35.33	1.500%	0.948%	0.454%	3.972%
	15	96.92%	20.14	1.615%	0.896%	0.381%	3.481%
	22.5	100.00%	13.61	1.807%	0.894%	0.416%	3.549%
DPMSAA-0.45-1.5X2C (2 ML)	3.75	62.82%	51.50	1.533%	1.030%	0.523%	4.535%
	7.5	87.35%	35.25	1.542%	0.942%	0.448%	4.101%
	11.25	94.30%	25.66	1.571%	0.915%	0.414%	3.793%
DPMSAA-0.45/0.30-1.5X2C (2 ML)	2.5	57.60%	66.41	1.480%	0.902%	0.709%	4.875%
	5	77.51%	44.63	1.530%	0.883%	0.683%	4.540%
	7.5	87.41%	34.38	1.520%	0.846%	0.600%	4.208%
DPMSAA-0.45NW-1.5X2C (2 ML)	3.75	63.00%	54.30	1.501%	0.824%	0.693%	4.538%
	7.5	84.20%	36.13	1.531%	0.808%	0.610%	4.034%
	11.25	93.44%	26.46	1.578%	0.802%	0.539%	3.707%
DPMSAA-0.25-1.5X2C (2 ML)	3.75	67.68%	52.61	1.565%	0.952%	0.399%	4.190%
	7.5	85.79%	33.77	1.552%	0.873%	0.405%	3.725%
	11.25	92.42%	24.34	1.623%	0.862%	0.412%	3.601%
DPMSAA-0.10-1.5X2C (2mL)	3.75	59.7%	50.28	1.666%	0.828%	0.267%	3.790%
	7.5	77.5%	32.51	1.660%	0.801%	0.330%	3.580%
	11.25	85.64%	24.05	1.670%	0.777%	0.315%	3.440%
Note: "2 ML" means flow was 2 ml/min - otherwise flow was 1 ml/min							

% was percent
conv. was conversion
prod. was product Bisphenol A
op/pp was the ratio of ortho, para bisphenol to para, parabisphenol tris was higher
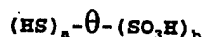oligomeric adduct derived from the reaction of 2 acetone molecules with 3 phenol molecules
cyclics were by-products having dianins, spirobiindanols, and dihydroindanols.

tot. imp. was total impurities including ortho, para bisphenol A, tris, cyclics as well as
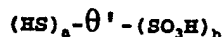
other unidentified product peaks.

WHAT IS CLAIMED IS:

1.   A process for the condensation of an aldehyde or ketone
starting material with a phenol, unsubstituted in at least one position,
wherein the aldehyde or ketone starting material is reacted with the
5   phenol in a reaction mixture in the presence of a soluble or insoluble
mercaptosulfonic acid compound under conditions sufficient to bring about
formation of a geminal bisphenolic moiety at each aldehyde or ketone
moiety in the starting material;

provided that the soluble mercaptosulfonic acid compound was
10   characterized by the formula

$$(HS)_a-\theta-(SO_3H)_b$$

wherein θ was an alkylene, cycloaliphatic, arylene, alkylenearylene,
alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic
residue and a and b were independently selected from integers from 1 to
15   20; and

the insoluble mercaptosulfonic acid comprises a catalytically-active
species represented by the formula

$$(HS)_a-\theta'-(SO_3H)_b$$
$$|$$
$$L$$
$$|$$

20

in which θ' was an alkylene, cycloaliphatic, arylene, alkylenearylene,
alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic
25   residue; a and b were independently selected from integers from 1 to 20; L
was an optional linking group and - was a bond, which catalytically-
active species was attached by the bond - to an insoluble organic or
inorganic support;

or a catalytically-active species represented by the unit formula
30                          $$(HS)_a \quad (SO_3H)_b$$
$$\backslash \quad /$$
$$-[\quad \theta'' - L']-$$

wherein θ'' was an alkylene, arylene, cycloaliphatic, alkylenearylene,
alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic
35   residue; a and b were independently selected from integers from 1 to 20;
L' was an optional linking group and - was a bond, wherein the
mercaptosulfonic acid catalyzes isomerization of crude product mixture to

produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization..

2.   The process of Claim 1, wherein the mercaptosulfonic acid compound was soluble in the reaction mixture and was characterized by the formula
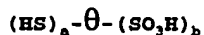
$$(HS)_a-\theta-(SO_3H)_b$$
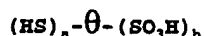
wherein θ was an alkylene, cycloaliphatic, arylene, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue and a and b were independently selected from integers from 1 to 10, wherein the mercaptosulfonic acid catalyzes isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization.

3.   The process of Claim 1, wherein the ketone was fluorenone, the phenol was unsubstituted and the product was 9,9-bis-(4-hydroxyphenyl)fluorene, wherein the mercaptosulfonic acid catalyzes isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization.

4.   The process of Claim 2, comprising a process for making a bisphenol by the step of contacting an aldehyde or a ketone with excess phenolic compound in the presence of a catalytic amount of mercaptosulfonic acid catalyst, which was soluble in the reaction mixture, at a temperature selected such that a bisphenol was formed and crystallizes in the reaction mixture, wherein the mercaptosulfonic acid catalyzes isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization.

5.   The process of Claim 4, wherein the ketone was acetone, the phenolic compound was phenol, and the bisphenol was bisphenol A, wherein the mercaptosulfonic acid catalyzes isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization..

6.   The process of Claim 1, wherein the catalyst was represented by the formula

$$(HS)_a-\theta-(SO_3H)_b$$

wherein θ was an alkylene, cycloaliphatic, arylene, alkylenearylene, alkylene-cycloaliphatic, alkylene-aryl, heterocyclic, or alkylene-heterocyclic moiety, and a and b were each independently integers averaging from 1 to 4, wherein the mercaptosulfonic acid catalyzes

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isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization..

7.   The process of Claim 6, wherein the catalyst was represented by the formula

$$(HS)-\theta-(SO_3H)$$

wherein θ was an alkylene, cycloalkylene or arylene moiety having from 2 to 10 carbon atoms, wherein the mercaptosulfonic acid catalyzes isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization.

8.   The process of Claim 1, wherein the mercaptosulfonic acid was an insoluble material comprising a catalytically-active species represented by the formula

$$(HS)_a-\theta'-(SO_3H)_b$$
$$|$$
$$L$$
$$|$$

in which θ' was an alkylene, cycloaliphatic, arylene, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were independently selected from integers from 1 to 20; L was an optional linking group and - was a bond, which catalytically-active species was attached by the bond - to an insoluble organic or inorganic support;

or a catalytically-active species represented by the unit formula

$$(HS)_a \quad (SO_3H)_b$$
$$\backslash \quad /$$
$$-[\quad \theta'' - L']-$$

wherein θ'' was an alkylene, arylene, cycloaliphatic, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were independently selected from integers from 1 to 5; L' was an optional linking group and -was a bond, wherein the mercaptosulfonic acid catalyzes isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization.

9.   The process of Claim 8, wherein the catalytically-active species was attached to the backbone of a polymer from at least one ethylenic monomer, wherein the mercaptosulfonic acid catalyzes

isomerization of crude product mixture to produce more bis-(4-
hydroxyphenyl) compound than would be produced without isomerization..

10.   The process of Claim 8, wherein the catalytically-active
species was incorporated in a polystyrene resin, wherein the
mercaptosulfonic acid catalyzes isomerization of crude product mixture to
produce more bis-(4-hydroxyphenyl) compound than would be produced without
isomerization..

11.   The process of Claim 10, wherein the polystyrene resin
includes unit structures represented by the formula

B
|
$CRSO_3H$
|
C_nH_{2n}
|
CHR^1SH
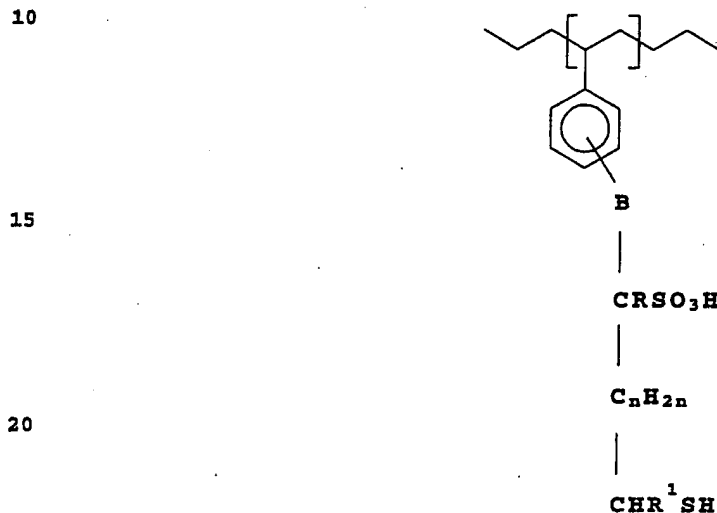
wherein B was a bridging group, R and R^1 were independently selected from
H, alkyl and aryl, $-C_nH_{2n}-$ was straight or branched chain alkylene and n
was an integer from 0 to 20, wherein the mercaptosulfonic acid catalyzes
isomerization of crude product mixture to produce more bis-(4-
hydroxyphenyl) compound than would be produced without isomerization.

12.   The process of Claim 10, wherein the polystyrene resin was
made by the steps of

(a)   treating polystyrene with an alkenyl halide of the formula
$RC(R^1)=C(R^2)C_mH_{2m}CH(R^3)X$, wherein R, R^1, R^2 and R^3 were independently
selected from H, alkyl or aryl; X was selected from F, Cl, Br or I and m
was 0 to 10; to produce a haloalkylpolystyrene;

(b)   sulfonating the resulting haloalkylpolystyrene to produce a
sulfo(haloalkyl)polystyrene,

(c)   optionally converting the sulfo function to an alkali metal or alkaline earth metal salt,

(d)   reacting the halo function with a reactive thiolate to produce a corresponding mercaptan function and

(e)   optionally acidifying to produce a corresponding sulfonic acid function,

(f)   isomerizatizing crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization in the presence of the mercaptosulfonic acid.

13.   The process of Claim 12, wherein the alkenyl halide was an allyl halide of the formula $RC(R^1)=C(R^2)CH(R^3)X$, wherein each of R, R^1, R^2 and R^3 was H independently H or alkyl of 1-5 carbon atoms.

14. The process of Claim 10, wherein the polystyrene resin includes unit structures represented by the formula
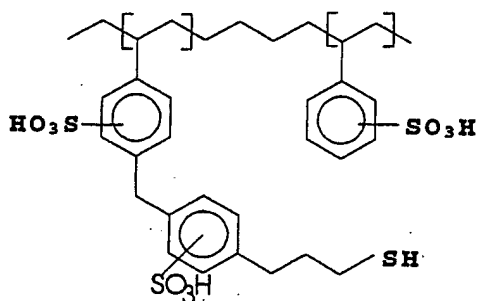
wherein the mercaptosulfonic acid catalyzes isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization.

15.   The process of Claim 10, wherein the polystyrene resin was made by the steps of:

(a)   alkylating a haloalkylated polystyrene with a haloalkylarylene compound to produce an intermediate having [(haloalkyl)phenylalkyl] styrene units;

(b)   sulfonating the tus-produced intermediate to produce an intermediate containing [(haloalkyl)(sulfo)phenylalkyl] sulfostyrene units;

(c)   optionally converting the sulfo functions to corresponding alkali metal salts;

(d)   thiolating the thus-produced intermediate which contained sulfostyrene units;

(e)   and hydrolyzing the thus-thiolated intermediate with an acid to produce a polymer containing [(mercaptoalkyl)(sulfo)-phenylalkyl) sulfopolystyrene units.

16.   The process of Claim 10, wherein the polystyrene resin was made by the steps of (a) reacting a haloalkystyrene polymer with a lithiated sultone, (b) treating a resulting sultone-functionalized polymer with a reactive thiolate and (c) acidifying the resulting intermediate to produce a polymer containing (mercaptosulfoalkyl)styrene units.

17.   A process to make a bisphenol, wherein an aldehyde or a ketone is contacted with excess phenolic compound in the presence of a catalytic amount of a mercaptosulfonic acid catalyst, which was soluble in the reaction mixture, at a temperature selected such that a bisphenol was formed and crystallizes in the reaction mixture and wherein the mercaptosulfonic acid catalyzes isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization.

18.   The process of Claim 15, wherein the catalyst was represented by the formula:
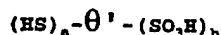
$$(HS)_a - \theta' - (SO_3H)_b$$

wherein θ was an alkylene, cycloaliphatic, arylene, alkylene-arylene, alkylene-cycloaliphatic, alkylene-aryl, heterocyclic, or alkylene-heterocyclic moiety, and a and b were each independently integers averaging from 1 to 4.

19.   The process of Claim 15, wherein the mercaptosulfonic acid catalyzes isomerization of crude product mixture to produce more bis-(4-hydroxyphenyl) compound than would be produced without isomerization.

20.   A process of isomerizing an o,p-bisphenol to form a corresponding p,p-bisphenol wherein the o,p-bisphenol is contacted with a mercaptosulfonic acid at a temperature sufficient to result in isomerization of the o,p-bisphenol to form a p,p-bisphenol.

$$(HS)_a - \theta - (SO_3H)_b$$

wherein θ was an alkylene, cycloaliphatic, arylene, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue and a and b were independently selected from integers from 1 to 20; and

5　the insoluble mercaptosulfonic acid comprises a catalytically-active species represented by the formula

$$(HS)_a-\theta'-(SO_3H)_b \tag{a}$$
$$|$$
$$L$$
10　$$|$$

in which θ' was an alkylene, cycloaliphatic, arylene, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were independently selected from integers from 1 to 20; L

15　was an optional linking group and - was a bond, which catalytically-active species was attached by the bond - to an insoluble organic or inorganic support;

　　or a catalytically-active species represented by the unit formula

$$(HS)_a \quad (SO_3H)_b$$
20　$$\backslash \quad /$$
$$-[\quad \theta'' - L']- \tag{b}$$
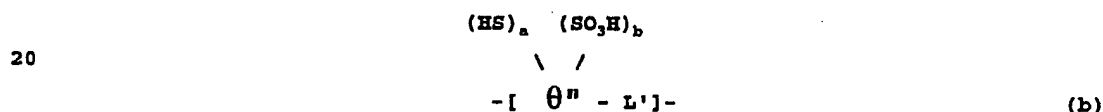
wherein θ'' was an alkylene, arylene, cycloaliphatic, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were independently selected from integers from 1 to 20;

25　L' was an optional linking group and - was a bond.

　　　21.　The process of Claim 20, wherein the mercaptosulfonic acid compound was soluble in the reaction mixture and was characterized by the formula

$$(HS)_a-\theta-(SO_3H)_b$$
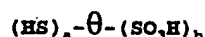
30　wherein θ was an alkylene, cycloaliphatic, arylene, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue and a and b were independently selected from integers from 1 to 10.

　　　22.　The process of Claim 20, wherein each of a and b were

35　independently selected from integers from 1 to 4.

　　　23.　The process of Claim 20, wherein a and b were each 1.

24.   The process of Claim 20, wherein the mercaptosulfonic acid compound was generated in the reaction mixture by reaction between an alkali metal salt of a mercaptosulfonic acid and a mineral acid.

25.   The process of Claim 24, wherein the alkali metal salt of the mercaptosulfonic acid compound was generated in the reaction mixture by reaction between a mercaptosulfonate ester and an alkali metal hydroxide.

26.   The process of Claim 22, wherein the mercaptosulfonic acid compound was generated in the reaction mixture by reaction between a mercaptosulfonyl halide and a mineral acid.

27.   The process of Claim 21, wherein the mercaptosulfonic acid compound was a mercaptoalkanesulfonic acid of up to 20 atoms between the mercapto and sulfonic acid groups.

28.   The process of Claim 21, wherein the mercaptosulfonic acid compound was 3-mercaptopropanesulfonic acid.

29.   The process of Claim 21, wherein the mercaptosulfonic acid compound was 4-mercaptobutanesulfonic acid.

30.   The process of Claim 21, wherein the mercaptosulfonic acid compound was 2-mercaptoethanesulfonic acid.

31.   The process of Claim 21, wherein the mercaptosulfonic acid was free of or substantially free of chloride ions.

32.   The process of Claim 20, carried out at a temperature from 15°C to 60°C.

33.   The process of Claim 20, wherein the reaction mixture contained from 0.01 to 2.0 equivalent of mercaptosulfonic acid per mole of aldehyde or ketone.

34.   The process of Claim 20, carried out with removal of water from the reaction mixture.

35.   The process of Claim 20, wherein the reaction mixture contained from 0.02 to 1.0 equivalent of mercaptosulfonic acid per mole of aldehyde or ketone.

36.   The process of Claim 20, wherein the ketone was fluorenone, the phenol was unsubstituted and the product was 9,9-bis-(4-hydroxyphenyl)fluorene.

37.   The process of Claim 20, wherein the ketone was acetone, the phenol was unsubstituted and the product was 2,2-bis-(4-hydroxyphenyl)propane.

38.   The process of Claim 20, wherein the ketone was 4-hydroxyacetophenone, the phenol was unsubstituted and the product was 1,1,1-tris-(4-hydroxyphenyl)ethane.
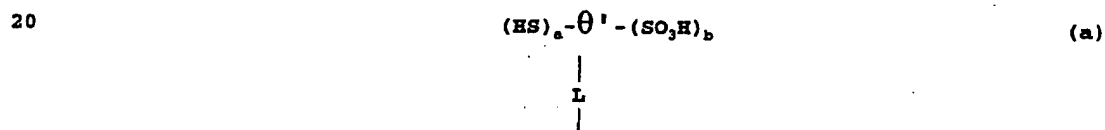
39.   The process of Claim 20, wherein crude product, resulting from
5   the condensation, was extracted with water to remove $(HS)_a-\theta-(SO_3H)_b$ from the product.

40.   The process of Claim 20, wherein crude product, resulting from the condensation, was extracted with an aqueous solution of an alkali metal hydroxide, carbonate or bicarbonate to remove $(HS)_a-\theta-(SO_3H)_b$ from
10   the product.

41.   The process of Claim 20, wherein crude product, resulting from the condensation, was treated with an anion-exchange resin to remove $(HS)_a-\theta-(SO_3H)_b$ from the product.
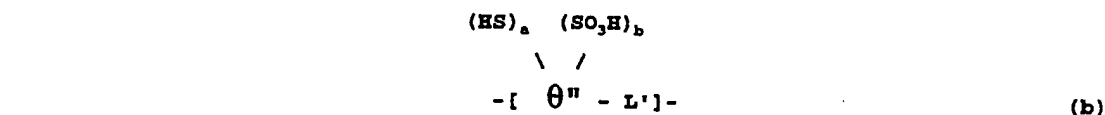
42.   The process of Claim 39, wherein the resulting aqueous extract
15   is further concentrated and the thus-concentrated solution of extracted $(HS)_a-\theta-(SO_3H)_b$ is recycled to the process.

43.   The process of Claim 20, wherein the mercaptosulfonic acid was an insoluble material comprising a catalytically-active species represented by the formula

20
$$(HS)_a-\theta'-(SO_3H)_b \qquad\qquad (a)$$
$$|$$
$$L$$
$$|$$

25   in which θ' was an alkylene, cycloaliphatic, arylene, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were independently selected from integers from 1 to 20; L was an optional linking group and -was a bond, which catalytically-active species was attached by the bond - to an insoluble organic or inorganic
30   support;

   or a catalytically-active species represented by the unit formula

$$(HS)_a \quad (SO_3H)_b$$
$$\backslash \quad /$$
$$-[\quad \theta'' - L']- \qquad\qquad (b)$$

35   wherein θ'' was an alkylene, arylene, cycloaliphatic, alkylenearylene, alkylenecycloaliphatic, alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were independently selected from integers from 1 to 5; L' was an optional linking group and -was a bond.

44.   The process of Claim 43, wherein the catalytically-active species was attached to the backbone of a polymer from at least one ethylenic monomer.

45.   The process of Claim 43, wherein the catalytically-active species was incorporated in a polystyrene resin.

46.   The process of Claim 45, wherein the polystyrene resin includes unit structures represented by the formula

$$\begin{array}{c} \text{B} \\ | \\ \text{CRSO}_3\text{H} \\ | \\ \text{C}_n\text{H}_{2n} \\ | \\ \text{CHR}^1\text{SH} \end{array}$$
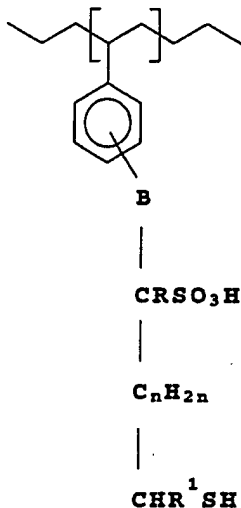
wherein B was a bridging group, R and R^1 were independently selected from H, alkyl and aryl, $-C_nH_{2n}-$ was straight or branched chain alkylene and n was an integer from 0 to 20.

47.   The process of Claim 46, wherein B was CH_2 and $-C_nH_{2n}-$ was $-CH_2CH_2-$ or $-CH_2-$.

48.   The process of Claim 45, wherein the polystyrene resin was made by the steps of

(a)   treating polystyrene with an alkenyl halide of the formula $RC(R^1)=C(R^2)C_mH_{2m}CH(R^3)X$, wherein R, R^1, R^2 and R^3 were independently selected from H, alkyl or aryl; X was selected from F, Cl, Br or I and m was 0 to 10; to produce a haloalkylpolystyrene;

(b)   sulfonating the resulting haloalkylpolystyrene to produce a sulfo(haloalkyl)polystyrene,

(c)   optionally converting the sulfo function to an alkali metal or alkaline earth metal salt,

(d)   reacting the halo function with a reactive thiolate to produce
a corresponding mercaptan function and

(e)   optionally acidifying to produce a corresponding sulfonic acid
function.

49.   The process of Claim 48, wherein the alkenyl halide was an
allyl halide of the formula $RC(R^1)=C(R^2)CH(R^3)X$, wherein each of R, R^1, R^2
and R^3 was H independently H or alkyl of 1 to 5 carbon atoms.

50.   The process of Claim 49, wherein each of R, R^1 and R^2 was H.

51.   The process of Claim 48, wherein the alkenyl halide was 5-
bromo-1-pentene or 11-bromo-1-undecene.

52.   The process of Claim 49, wherein the polystyrene resin
includes unit structures represented by the formula
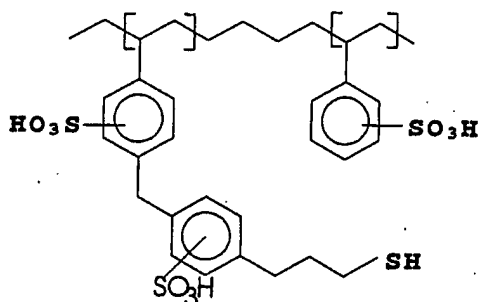
53.   The process of Claim 49, wherein the ketone was fluorenone,
the phenol was unsubstituted and the product was 9,9-bis-(4-hydroxyphen-
yl)fluorene.

54.   A catalytically-active material characterized in that there is
an insoluble organic or inorganic support in which is incorporated a mer-
captosulfonic acid residue represented by the formula

$$(HS)_a - \theta' - (SO_3H)_b$$
$$|$$
$$L$$
$$|$$
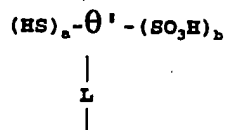
in which θ' was an alkylene, cycloaliphatic, arylene, alkylenearylene,
alkylenearyl, heterocyclic or alkyleneheterocyclic residue; a and b were
independently selected from integers from 1 to 20; L was an optional

linking group and - was a bond, which catalytically-active species was
attached by the bond - to the insoluble organic or inorganic support.

55. The process of Claim 20, carried out in a stainless steel
reactor, wherein the corrosion rate of the stainless steel reactor was
less than 0.00254 cm/year.

56. The process of Claim 31, carried out in a stainless steel
reactor, wherein the corrosion rate of the stainless steel reactor was
less than 0.00254 cm/year.

57. The process of Claim 20, carried out in the absence of a
diluent, other than excess phenol.

58. The process of Claim 20, carried out in the presence of
diphenylmethane as a diluent.

59. The process of Claim 43, including the further steps of
separating the catalytically-active material from the mixture; washing the
catalytically-active material with a mixture of phenol and aldehyde or
ketone and recycling the thus-washed material to the process.

60. The process of Claim 20, carried out in a batch reactor.

61. The process of Claim 20, carried out in a continuous reactor.

62. The process of Claim 37, carried out in the presence of a
diluent which forms an adduct with 2,2-bis-(4-hydroxy-phenyl)propane under
conditions such that 2,2-bis-(4-hydroxy-phenyl)propane crystallizes in the
reaction mixture.

63. The process of Claim 45, wherein the polystyrene resin was
made by the steps of:

(a) alkylating a haloalkylated polystyrene with a
haloalkylarylene compound to produce an intermediate having
[(haloalkyl)phenylalkyl] styrene units;

(b) sulfonating the thus-produced intermediate to produce an
intermediate containing [(haloalkyl)(sulfo)phenylalkyl] sulfostyrene
units;

(c) optionally converting the sulfo-functions to
corresponding alkali metal salts;

(d) thiolating the thus-produced intermediate which
contained sulfostyrene units;

(e) and hydrolyzing the thus-thiolated intermediate with an
acid to produce a polymer containing [(mercaptoalkyl)(sulfo)-phenylalkyl)
sulfopolystyrene units.

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64.   The process of Claim 63, wherein the haloalkylarylene compound was selected from   chlorobenzene, chloromethylbenzene, chloroethylbenzene, chloropropylbenzene, chlorobutylbenzene or corresponding fluoro, bromo or iodo analogues.

5   65.   The process of Claim 64, wherein the haloalkylarylene compound was selected from bromobenzene, bromomethylbenzene, bromoethylbenzene, bromopropylbenzene or bromobutylbenzene.

66.   The process of Claim 45, wherein the polystyrene resin was made by the steps of (a) reacting a haloalkystyrene polymer with a

10   lithiated sultone, (b) treating a resulting sultone-functionalized polymer with a reactive thiolate and (c) acidifying the resulting intermediate to produce a polymer containing (mercaptosulfoalkyl)styrene units.

67.   The process of Claim 66, wherein the lithiated sultone was a lithiated 1,3-propanesultone.

15   68.   The process of Claim 66, wherein the lithiated sultone was a lithiated 1,4-butanesultone.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C07C 39/16
US CL :568/727, 728, 722, 723, 717

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 568/727, 728, 722, 723, 717

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	US 5,463,140 A (WEHMEYER et al.) 31 October 1995, entire document.	1-68
A	US 2,923,744 A (SCRIABINE et al.) 02 February 1960, entire document.	1
A	US 4,675,458 A (RIEMANN et al.) 23 June 1987, entire document.	1
A	US 4,996,373 A (BOTTENBRUCH et al.) 26 February 1991, entire document.	1
A	US 5,248,838 A (MASSIRIO et al.) 28 September 1993, entire document.	1

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 NOVEMBER 1996	03 DEC 1996
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer SREENI PADMANABHAN
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